A SYNERGISTIC SYNTHETIC, SPECTROSCOPIC AND COMPUTATIONAL APPROACH TO THE DESIGN OF ORGANOMETALLIC PLATFORMS FEATURING LINEARLY FUNCTIONALIZED AZULENIC AND BIAZULENIC MOTIFS

By

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Submitted to the graduate degree program in Chemistry and the Graduate Faculty of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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A SYNERGISTIC SYNTHETIC, SPECTROSCOPIC AND COMPUTATIONAL APPROACH TO THE DESIGN OF ORGANOMETALLIC PLATFORMS FEATURING LINEARLY FUNCTIONALIZED AZULENIC AND BIAZULENIC MOTIFS

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Abstract

While there is great interest in using small organic molecules in everything from organic light emitting diodes to charge transport in molecular electronics, finding the right scaffold for development has posed substantial challenges. Linear azulenic motifs have proven the ability to delocalize electrons and demonstrate unique photoluminescence properties. Continuing the development of functionalized azulenes in the Barybin group, this dissertation describes the explorations into mercapto- and isocyano- azulenes and biazulenes. With a diverse toolkit, the dynamics, materials, energy, reactivity, and spectroscopy of these systems have been described.

In Chapter 1, the preparation, X-ray crystal structures, theoretical models, reactivities, and photoluminescent behavior of the mercapto-azulene ligands and gold(I) complexes involving 2- and 6-azulenyl thiolate motifs are discussed. These novel compounds constitute attractive platforms for developing new photoluminescent materials and, possibly, metallopharmaceuticals.

In Chapter 2, 2,6-dimercapto-1,3-diethoxycarbonylazulene, a rare example of an unsymmetric dimercaptoarene, was computationally determined to be an excellent system to undergo regioselective metallation. The [Ph_3PAu^I] metalated complex was shown to have very dynamic behavior using NMR studies. This complex constitutes a unique unsymmetric platform for probing the exchange of gold-bound thiolates within a single compound.

In Chapter 3, linear, functionalized 6,6'-biazulenyl's were synthesized in excellent yields. Unusual $2e^-$ redox behavior was addressed electrochemically and computationally. The reduced anionic and dianionic states were explored using theoretical, EPR, and UV-Vis-NIR methods.

Acknowledgements

A great deal of thanks needs to go out to a great deal of people. As it seems fashionable to recognize your academic family tree, let me recognize my 'scientific aunts and uncles'.

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To my parents (Doug & Karen) and extended family, you helped me achieve my dreams. Thank you also to my 'adopted' parents (Bob & Marilyn) and their family. To my wife, Erin, you probably didn't quite know what you were marrying, but I'm grateful you did. Also, to Garik who has been a great blessing in our lives.

And very lastly, I dedicate this dissertation in memoriam to my grandfather, James S. Ekstrand (retired from Abbott Laboratories). You are the reason I have an insatiable thirst for knowledge, a large personal library, and why I choose chemistry.

Table of Contents

List of Tables

Chapter 1

Chapter 2

Chapter 3

List of Figures

Chapter 1

Chapter 2

Chapter 3

List of Schemes

Chapter 1

Chapter 2

Chapter 3

Abbreviations Used

2-MeTHF – 2-Methyl-tetrahydrofuran

BHT – Butylated hydroxytoluene

$CoCp_2^*$ – Decamethylcobaltocene

CV – Cyclic voltammetry

dcpm – Bis(dicyclohexylphosphino)methane

DBU – Diazabicyclo[5.4.0]undec-7-ene

DFT – Density functional theory

DMSO – Dimethylsulfoxide

EPR – Electron paramagnetic resonance

FTIR – Fourier transform infrared spectroscopy

HOMO – Highest occupied molecular orbital

HRMS – High resolution mass spectrometry

ILCT – Intra-ligand charge-transfer

LUMO – Lowest unoccupied molecular orbital

MLCT – Metal-to-ligand charge-transfer

NIR – Near-infrared

NMR – Nuclear magnetic resonance

Opt – Geometric optimization

ORTEP – Oak Ridge thermal ellipsoid plot

SAM – Self-assembled monolayer

SARB – Side-armed round-bottomed flask

SOMO – Singly-occupied molecular orbital

SP – Single point energy

TD-DFT – Time-dependent density functional theory

THF – Tetrahydrofuran

UV – Ultraviolet

Vis – Visible

CHAPTER 1

Synthesis, Reactivity, and Photoluminescence of Mercaptoazulenes and their Complexes with Gold(I)

Abstract

Azulenic compounds often exhibit unusual photophysical properties, in part, due to their emission from the second singlet excited state, which violates Kasha's Rule. Surprisingly, while the syntheses of several mercaptoazulene derivatives had been published decades ago, the chemistry of these functionalized azulenes as ligands in transition metal coordination complexes remained completely unexplored until very recent studies in the Barybin group. The preparation, X-ray crystal structures, theoretical models, reactivities, and photoluminescent behavior of the ligands and gold(I) complexes involving 2- and 6-azulenyl thiolate motifs are discussed. These novel compounds constitute attractive platforms for developing new photoluminescent materials and, possibly, metallopharmaceuticals.

Introduction

Azulene, a bicyclic, non-benzenoid aromatic hydrocarbon $C_{10}H_8$ featuring fused 5- and 7-membered carbon rings, has fascinated chemists through the years by its stunning color and unusual physicochemical properties. Due to the decreased Highest Occupied Molecular Orbital – Lowest Unoccupied Molecular Orbital (HOMO–LUMO) gap, azulene has a deep blue color, which radically contrasts with its isomer naphthalene (colorless). The derivatives of azulene show all the colors of the rainbow by simple functionalization with electron donating or withdrawing substituents throughout the ring system.[1-8] Tuning of the azulene electronics by derivatization allows for control of the energies of both the first singlet (S_1) and second singlet (S_2) excited states in the molecule. This has made azulene a very attractive platform for many applications: from optoelectronic molecular switches[9] to nonlinear chromophores.[10,11]

Another unique feature of azulene and its derivatives is the unusual photoluminescence behavior of these compounds. Originally postulated by Prof. Michael Kasha in 1950,[12] Kasha's Rule states that molecules excited in condensed phases will always vibrationally relax to the first singlet excited state (S_1), and from there, will relax, via photon emission, back down to the ground state (S_0). This rule has been remarkably accurate with few exceptions that have been documented.[13,14] The classical exception to Kasha's Rule is azulene's tendency to fluoresce from the S_2 state.[15,16] Since that discovery, various derivatives of azulene, e.g., 1,3-dihaloazulenes, have continued breaking this rule.[17-19]

A metal-based class of equally interesting luminescent systems is represented by gold(I) thiolate/phosphine coordination motifs. These complexes have been studied thoroughly over the years and appear to exhibit interesting reaction dynamics.[20-26] In most cases, these compounds feature an intense Metal-to-Ligand Charge-Transfer (MLCT) band in their electronic absorption spectra. Their luminescence is greatly impacted by the ability of the complexes to form gold···gold interactions (termed aurophilic).[27] Azulene derivatives have already been shown to act as sensitizers when complexed with lanthanide atoms for emission in the near-infrared (NIR) region.[28] By combining the unique fluorescence of azulenes with the large absorption profile of gold(I) phosphine complexes, new and interesting photoluminescence profiles were targeted.

Also of medicinal interest is a widely popular rheumatoid arthritis drug Auranofin (Ridaura®) based on the gold(I) phosphine thiolate motif, see Figure 1.[29-32] It is thought the gold(I) species is the 'active' ingredient, though a thorough mechanistic understanding of this drug's action remains elusive. Given that many azulenic derivatives are known to have anti-inflammatory properties (e.g., Azunol used in the Post-Operative Sore Throat (POST) treatment

following tonsillectomies see Figure 1)[33], the accessibility of gold(I) azulenylthiolate complexes may open new opportunities in the design of anti-inflammatory agents.

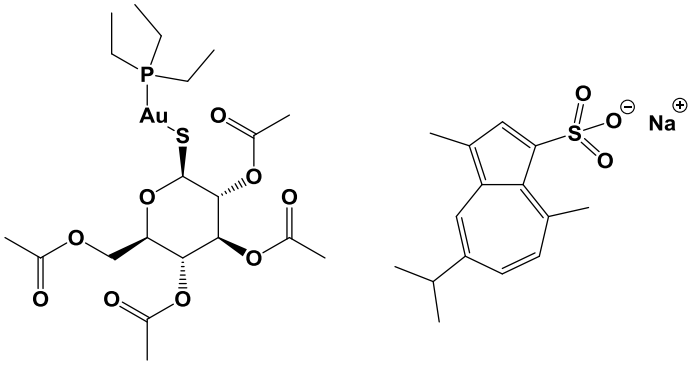
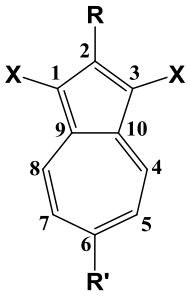


Figure 1: Structures of Auranofin (left) and Azunol (right).

This Chapter discusses the syntheses and comprehensive characterization of novel gold(I) phosphine azulenylthiolate complexes (see Scheme 1), as well as photophysical measurements and reactivity profiles involving the free mercaptoazulene ligands and their Au(I) complexes.



I.1a: R=SH, R'=H, X=CO_2Et
I.1b: R=SH, R'=H, X=H
I.1c: R=H, R'=SH, X=CO_2Et
I.1d: R=SH, R'=SH, X=CO_2Et
I.1e: R=SH, R'=2-azulenyl, X=CO_2Et

I.2a: R=SAuPPh$_3$, R'=H, X=CO_2Et
I.2b: R=SAuPPh$_3$, R'=H, X=H
I.2c: R=H, R'=SAuPPh$_3$, X=CO_2Et
I.2d: R=SH, R'=SAuPPh$_3$, X=CO_2Et
I.2e: R=SAuPPh$_3$, R'=SAuPPh$_3$, X=CO_2Et
I.2f: R=SAuPPh$_3$, R'=2-azulenyl, X=CO_2Et

Scheme 1: Numbering legend for the compounds discussed in this chapter and the carbon atom numbering scheme for the azulenic scaffold.

Experimental

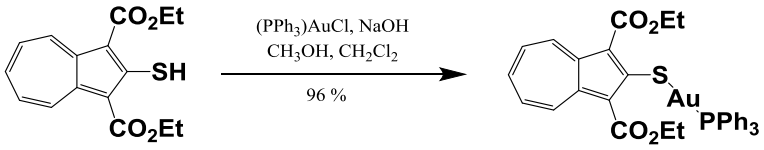
General procedures, starting materials and equipment.

Unless specified otherwise, all operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air. Solutions were transferred via stainless steel needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line. Both CH_2Cl_2 and CD_2Cl_2 were distilled over CaH_2. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Pentane was distilled from Na/benzophenone dissolved in a minimum amount of diglyme. Methanol was distilled over Mg turnings (activated by I_2). 2-Methyl-tetrahydrofuran (2-MeTHF) [stabilized with butylated hydroxytoluene (BHT)] was subjected to three freeze-pump-thaw cycles before use. Other solvents and chemicals were used as received from commercial sources.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with liquid samples sealed in 0.1 mm NaCl cells. NMR spectra were acquired on a 400 or 500 MHz Bruker DRX spectrometer equipped with a X-channel observe quadruple nuclei probe, or a 500 MHz Bruker AVIII spectrometer equipped with a cryogenically-cooled carbon observe probe. ^{1}H and ^{13}C NMR chemical shifts are given with reference to residual solvent resonances relative to $SiMe_4$. ^{31}P NMR chemical shifts are referenced externally to 85% aqueous H_3PO_4 (a sealed capillary tube containing 85% aqueous H_3PO_4 was inserted into each sample tube subject to ^{31}P NMR analysis). The Diffusion Ordered Spectroscopy (DOSY) NMR experiment was carried out according to the 'DOSY and Diffusion by NMR: a Tutorial for Topspin 1.3' manual (Bruker). The DOSY NMR spectral data were processed using the MestReNova (v.6) 'Bayesian DOSY

Transform' algorithm. UV-Vis spectra were recorded at 24 °C using a Cary 100 spectrophotometer at *ca.* 10^{-5} molar concentrations. Fluorescence spectra were obtained using a Cary Eclipse Fluorescence Spectrophotometer at *ca.* 10^{-5} molar concentrations and with excitation and emission slit widths set to 5 nm. The emission spectra were corrected for instrumental variation whenever possible (220 to 600 nm or 45,454 to 16,667 cm^{-1}). Low temperature operation for fluorescence and phosphorescence modes was achieved by using an Oxford OptistatDN cryostat under a nitrogen atmosphere. Phosphorescence spectra and lifetime measurements were obtained using a single lamp flash with a decay time of 0.02 s, delay time of 0.2 ms, and gate time of 5 ms. The lifetime measurements involved averaging 100 iterations and using an exponential function to fit the decay curve to determine the lifetime (τ). 2-Mercapto-1,3-diethoxycarbonylazulene (**I.1a**)[1], 2-mercaptoazulene (**I.1b**)[1], 6-mercapto-1,3-diethoxycarbonylazulene (**I.1c**)[4], 2,6-dimercapto-1,3-diethoxycarbonylazulene (**I.1d**)[4], 2-mercapto-1,3-diethoxycarbonyl-2',6-biazulene (**I.1e**)[34], PPh_3Au[1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate] (**I.2d**)[4], $[PPh_3Au]_2$(μ-1,3-diethoxycarbonyl-2,6-azulenedithiolate) (**I.2e**)[4], and $ClAuPPh_3$[35] were prepared according to literature procedures or minor variations thereof.

Synthesis of 2-thiolate-1,3-diethoxycarbonylazulene gold(I) triphenylphosphine (I.2a)



Scheme 2: Synthesis of **I.2a**.

2-Mercapto-1,3-diethoxycarbonylazulene, **I.1a** (0.055 g, 0.18 mmol), NaOH (0.041 g, 1.04 mmol), and $ClAuPPh_3$ [generated from $ClAu(SMe_2)$ (0.0511 g, 0.17 mmol) and PPh_3

(0.0455 g, 0.17 mmol)] were placed into a 100 mL SARB. To this mixture, 8 mL of methanol was transferred via cannula, and the resulting solution was stirred for 30 min at 25 ^{o}C with protection from ambient lighting. Then, 10 mL of CH_2Cl_2 was added and the solution was stirred at 25 ^{o}C for 24 hours with continuous protection from ambient lighting. All volatiles were removed under vacuum leaving an orange-red residue. A disposable pipette, filled with Celite® and a glass wool plug, was used to filter off any residual salts from the reaction using a minimum amount of additional CH_2Cl_2 to the filtercake. The collected red filtrate was concentrated and layered with pentane. Slow diffusion of pentane into the CH_2Cl_2 solution at -20 °C yielded 0.1316 g, 0.17 mmol (96%) of **I.2a** as red crystals. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ^{o}C) δ 8.69 (d, $^{3}J_{HH}$ = 10.0 Hz, 2H, *H* ^{4,8}), 7.60 – 7.41 (m, 18H, P*Ph*$_3$ + *H*^{5,6,7}), 4.22 (q, $^{3}J_{HH}$ = 7.1 Hz, 4H, -C*H*$_2$-), 1.31 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, -C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 ^{o}C) δ 167.09 (-*C*O$_2$-), 159.90, 141.69, 136.38, 134.79, 133.00, 132.25, 129.77, 129.67, 129.60, 122.06 (azulenic *C* and P*Ph*$_3$), 60.88 (-*C*H$_2$-), 14.81 (-*C*H$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): 36.49 ppm.

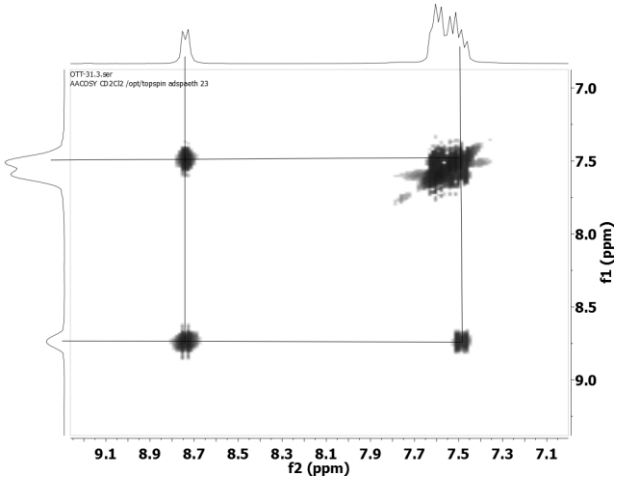
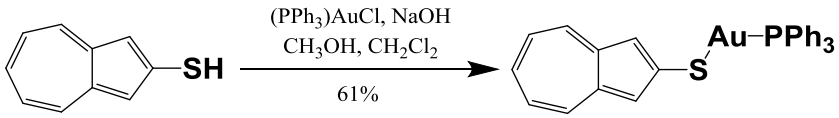


Figure 2: ^{1}H - ^{1}H correlated spectroscopy (COSY) NMR of **I.2a** used to help assign the observed peaks in its ^{1}H NMR spectrum.

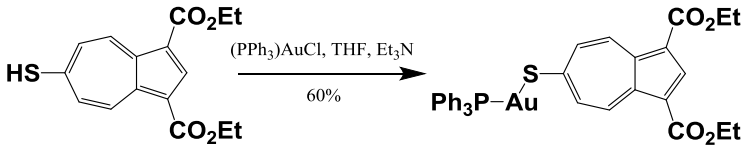
Synthesis of 2-thiolate-azulene gold(I) triphenylphosphine (I.2b)



Scheme 3: Synthesis of **I.2b**.

2-Mercapto-azulene, **I.1b** (0.0203 g, 0.12 mmol), NaOH (0.016 g, 0.4 mmol), and $ClAuPPh_3$ [generated from $ClAu(SMe_2)$ (0.0205 g, 0.070 mmol) and PPh_3 (0.0184 g, 0.070 mmol)] were placed into a 100 mL SARB. To this mixture, 8 mL of methanol was transferred via cannula and the resulting solution was stirred for 30 min at 25 ^{o}C with protection from ambient lighting. Then, 8 mL of CH_2Cl_2 was added, and the solution was stirred at 25 ^{o}C for 24 hours with continuous protection from ambient lighting. All volatiles were removed under vacuum leaving a brown residue. A disposable pipette, filled with Celite® and a glass wool plug, was used to filter off any residual salts from the reaction using CH_2Cl_2. The filtrate was layered with pentane. Slow diffusion of pentane into the CH_2Cl_2 solution at -20°C yielded 0.0265 g, 0.043 mmol (61 %) of **I.2b** as brown crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.86 (d, $^{3}J_{HH}$ = 9.6 Hz, 2H, $H^{4,8}$), 7.63 – 7.47 (m, 15 H, PPh_3), 7.33 (s, 2H, $H^{1,3}$), 7.27 (t, $^{3}J_{HH}$ = 9.8 Hz, 1 H, H^{6}), 7.05 (t, $^{3}J_{HH}$ = 9.7 Hz, 2H, $H^{5,7}$) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ 155.19, 140.79, 134.44, 134.33, 132.86, 131.90, 131.88, 130.27, 129.43, 129.34, 123.80, 121.16 (azulenic *C* and PPh_3) ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): 38.34 ppm.

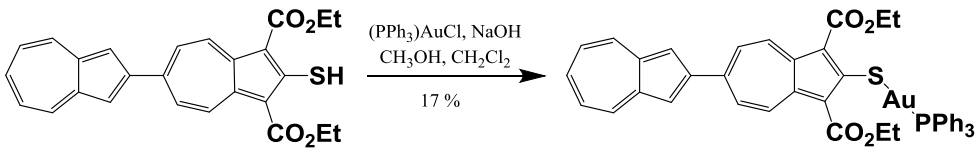
Synthesis of 6-thiolate-1, 3-diethoxycarbonylazulene gold(I) triphenylphosphine (I.2c)



Scheme 4: Synthesis of **I.2c**.

6-Mercapto-1,3-diethoxycarbonylazulene, **I.1c** (0.0519 g, 0.17 mmol) and $ClAuPPh_3$ [generated from $ClAu(SMe_2)$ (0.0501 g, 0.17 mmol) and PPh_3 (0.0441 g, 0.17 mmol)] were placed into a 100 mL SARB. To this mixture, 10 mL of THF was added, along with triethylamine (0.5 mL, 3.58 mmol). The resulting solution stirred at 25 ^oC for 24 hours with protection from ambient lighting. All volatiles were removed under vacuum leaving an orange-red residue. The residue was extracted with 50 mL CH_2Cl_2 and water (3 × 50 mL) in a separatory funnel. The organic layer was separated and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the filtrate was concentrated and layered with pentane. Slow diffusion of pentane into the CH_2Cl_2 solution at -20 °C yielded 0.0776 g, 0.10 mmol (60 %) of **I.2c** as red crystals. ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 9.20 (d, $^3J_{HH}$ = 11.3 Hz, 2H, $H^{4,8}$), 8.48 (s, 1H, H^2), 8.26 (d, $^3J_{HH}$ = 11.3 Hz, 2H, $H^{5,7}$), 7.60 – 7.48 (m, 15H, P*Ph*$_3$), 4.38 (q, $^3J_{HH}$ = 7.1 Hz, 4H, -C*H*$_2$-), 1.42 (t, $^3J_{HH}$ = 7.1 Hz, 6H, -C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 ^oC) δ 165.56 (-*C*O_2-), 140.99, 139.09, 135.30, 134.75, 134.30, 134.19, 132.18, 132.16, 129.61, 129.52, 129.10, 128.64, 115.82 (azulenic *C* and P*Ph*$_3$) 59.76 (-*C*H_2-), 14.72 (-*C*H_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): 37.98 ppm. FTIR (CH_2Cl_2): ν_{CO} 1685 s cm^{-1}.

Synthesis of 6-thiolate-1, 3-diethoxycarbonyl-2',6-biazulene gold(I) triphenylphosphine (I.2f)



Scheme 5: Synthesis of **I.2f**.

2-Mercapto-1,3-diethoxycarbonyl-2',6-biazulene, **I.1e** (0.056 g, 0.13 mmol), NaOH (0.0319 g, 0.78 mmol), and $ClAuPPh_3$ [generated from $ClAu(SMe_2)$ (0.0392 g, 0.13 mmol) and

PPh_3 (0.0344 g, 0.13 mmol)] were placed into a 100 mL SARB. To this mixture, 8 mL of methanol was transferred via cannula and the resulting solution was stirred at 25 ^oC for 30 min with protection from ambient lighting. Then, 10 mL of CH_2Cl_2 was added, and the solution was stirred at 25 ^oC for an additional 24 hours with protection from ambient lighting. All volatiles were removed under vacuum leaving a brown residue. A disposable pipette, filled with Celite® and a glass wool plug, was used to filter off any residual salts from the reaction using a minimum amount of additional CH_2Cl_2 to the filtercake. The filtrate was layered with pentane. Diffusion of pentane into the CH_2Cl_2 solution at -20°C yielded 0.0195 g, 0.022 mmol (17 %) of **I.2f** as a brownish-red solid. ^1H NMR (500 MHz, $CDCl_3$, 25.2^oC) δ 8.84 (d, $^3J_{HH}$ = 11.4 Hz, 2H, $H^{4,8}$), 8.24 (d, $^3J_{HH}$ = 9.2 Hz, 2H, $H^{4',8'}$), 8.09 (d, $^3J_{HH}$ = 11.2 Hz, 2H, $H^{5,7}$), 7.66 (s, 2H, $H^{1',3'}$), 7.56 – 7.41 (m, 16 H, $H^{6'}$ + PPh_3), 7.11 (t, $^3J_{HH}$ = 9.8 Hz, 2H, $H^{5',7'}$), 4.30 (q, $^3J_{HH}$ = 7.1 Hz, 4H, -CH_2-), 1.37 (t, $^3J_{HH}$ = 7.1 Hz, 6H, -CH_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25.2^oC) δ 166.77 (-CO_2-), 160.14, 151.59, 143.70, 141.31, 140.88, 137.67, 137.21, 134.28, 134.17, 131.82, 131.68, 131.66, 129.61, 129.46, 129.21, 129.16, 129.12, 124.29, 121.71, 115.94 (azulenic *C* and PPh_3), 60.31 (-CH_2-), 14.60 (-CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 20.8°C): 36.41 ppm.

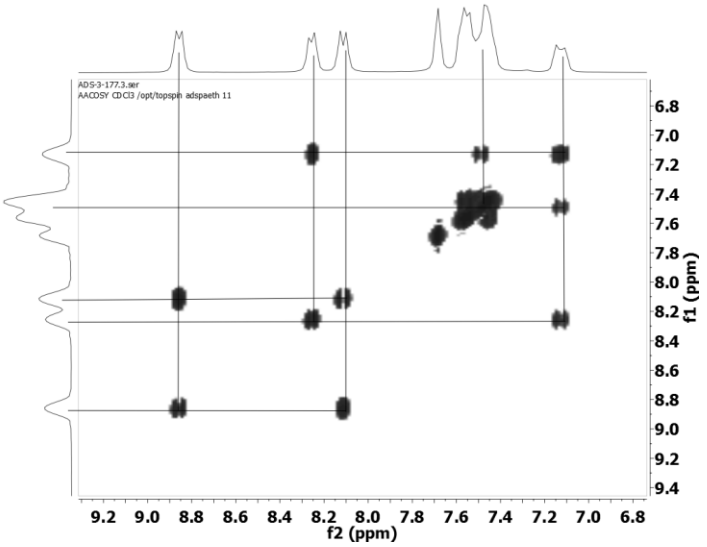


Figure 3: ^{1}H - ^{1}H correlated spectroscopy (COSY) NMR of **I.2f** used to help assign the observed peaks in its ^{1}H NMR spectrum.

Density Functional Theory Calculations

All density functional theory (DFT) calculations were performed using the ORCA (v.2.9.1 or 3.0) program.[36,37] Geometric optimizations and numerical frequency calculations were performed using the B3LYP functional with a triple-zeta valence with polarization (TZVP) basis set, the resolution of identity approximation (RI) 'chain of spheres' algorithm (RIJCOSX), and a TZV/J auxiliary basis set [Ahlrich's Coulomb fitting basis for TZVP].[38-43] When gold atoms were present, geometric optimizations were preformed with BP86, TZVP, TZV/J, the RI and the Zero-Order Regular Approximation (ZORA).[38,39,44-47] The BP86 functional was chosen for geometric optimizations as it has been shown to be quite accurate for inorganic systems[48], while B3LYP was chosen for the numerical frequency calculations to match the approach of Shields, *et al.*[49] No imaginary frequencies were observed after the numerical frequency calculation. The solvation effects of dimethylsulfoxide (DMSO) [ε = 47.2] were modeled using the conductor-like screening model (COSMO), as implemented in ORCA.[50] The final Cartesian

coordinates for all optimized structures are provided in the appendices, see Tables A1.1 – A1.59. From the numerical frequency calculations, the Gibb's Free Energy was obtained for the protonated and deprotonated species in both gas phase and in DMSO. These values were then plugged into Equations 1 & 2, *vide infra*. All calculations were documented in Tables A1.60 and A1.61. Orbital surface contour plots were produced using the gOpenMol (v.3.00) program with isodensity values set to ±0.05 for organic ligands and ±0.03 for gold(I) complexes.

Photoluminescence Results

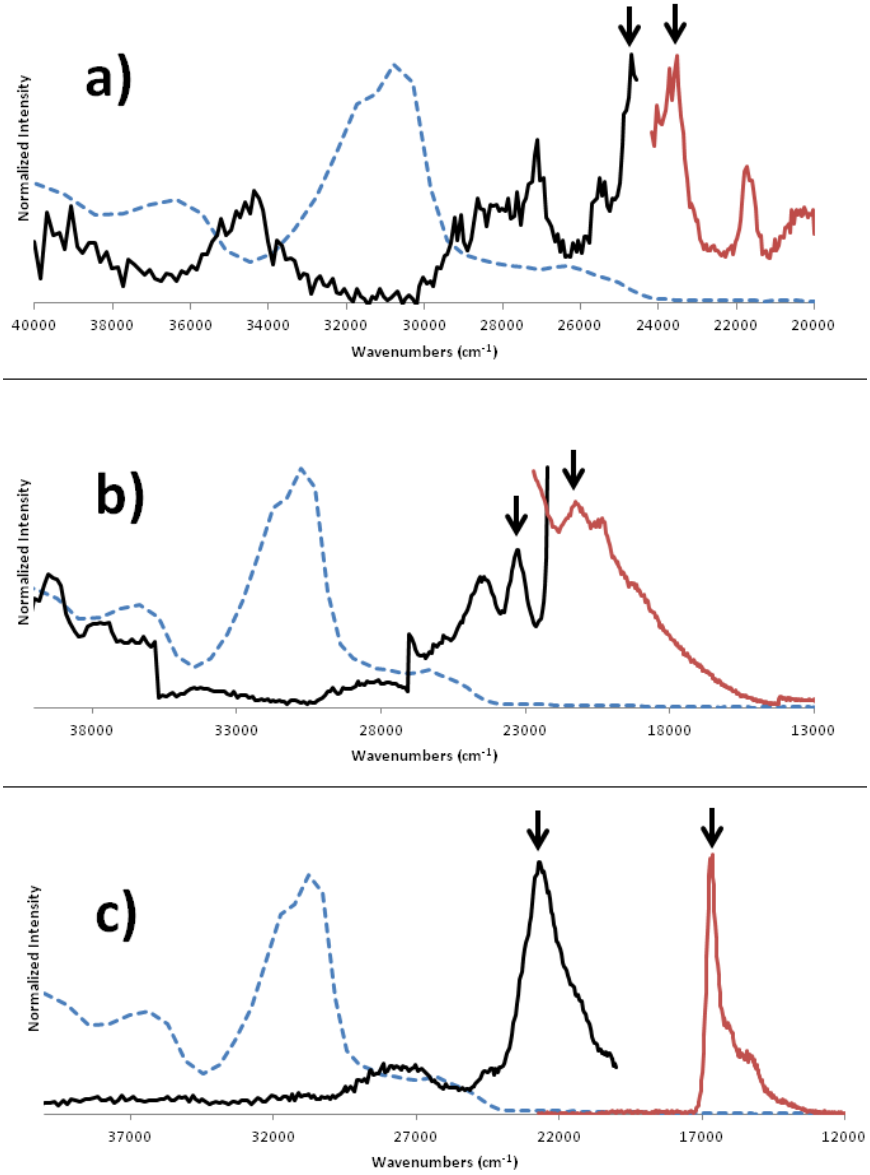


Figure 4: Fluorescence spectra of **I.1a** at 293 K in CH_2Cl_2 (a) and at 77 K in 2-MeTHF (b). Phosphorescence spectrum **I.1a** at 77 K in 2-MeTHF (c). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is the UV-Vis absorption spectrum (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

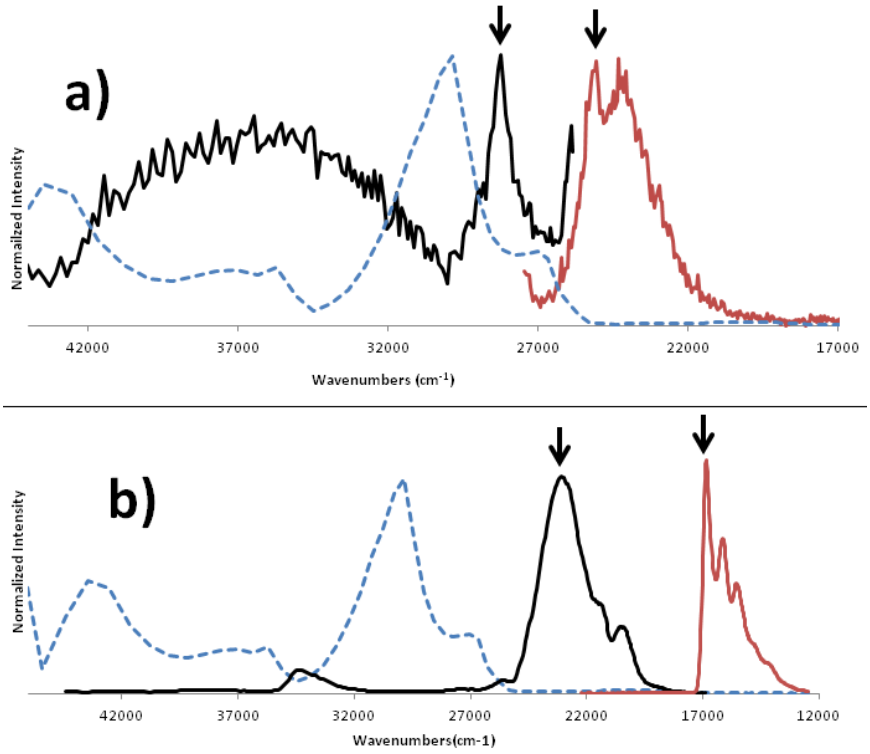


Figure 5: Fluorescence spectrum of **I.1c** at 293 K in CH_2Cl_2 (a). Phosphorescence spectrum of **I.1c** at 77 K in 2-MeTHF (b). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is UV-Vis the absorption spectrum (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

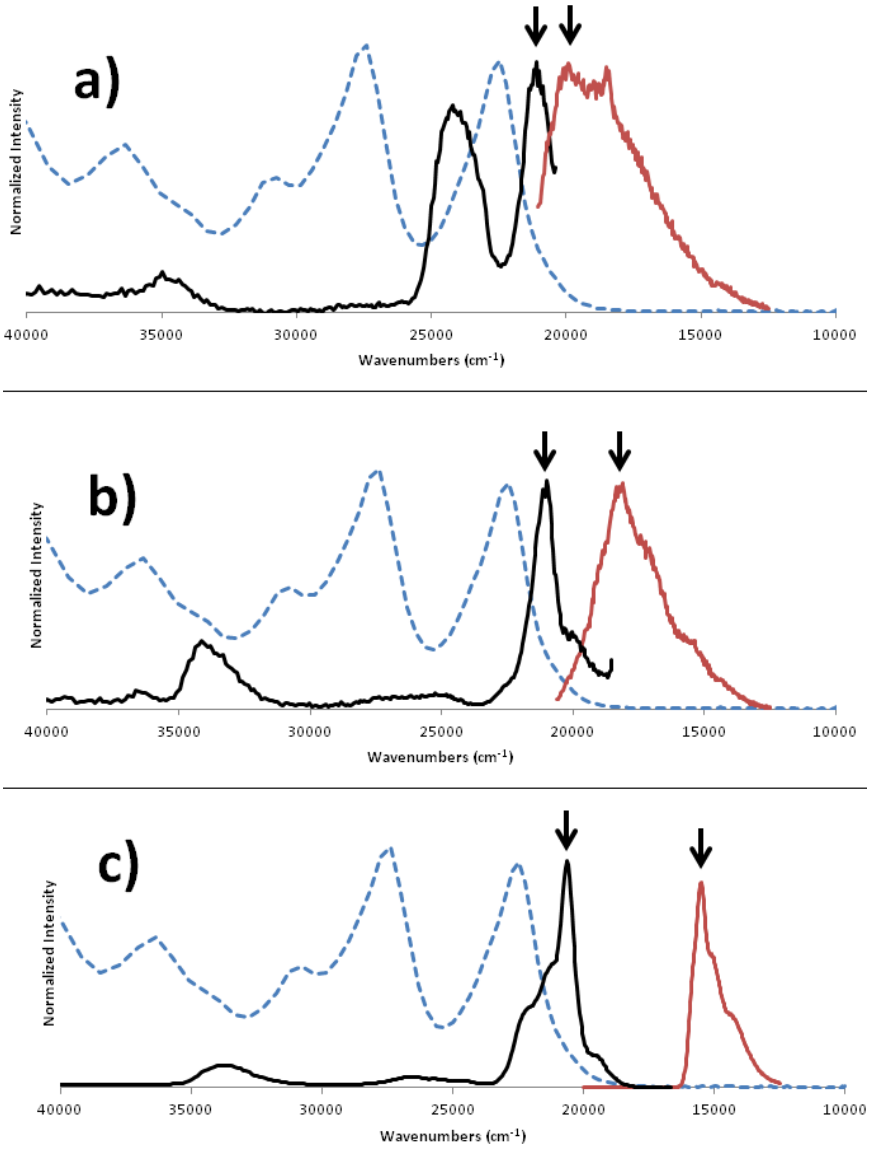


Figure 6: Fluorescence spectra of **I.1d** at 293 K in CH_2Cl_2 (a) and at 77 K in 2-MeTHF (b). Phosphorescence spectrum of **I.1d** at 77 K in 2-MeTHF (c). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is the UV-Vis absorption spectrum (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

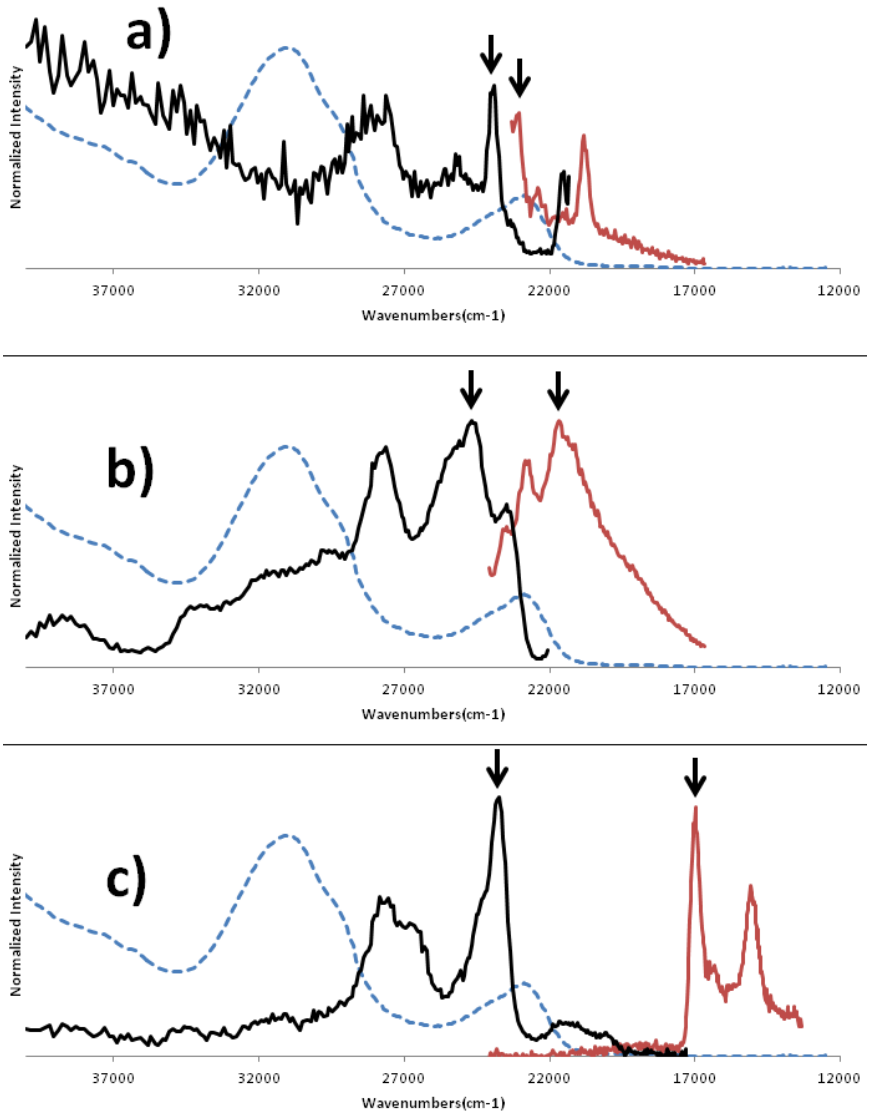


Figure 7: Fluorescence spectra of **I.2a** at 293 K in CH_2Cl_2 (a) and at 77 K in 2-MeTHF (b). Phosphorescence spectrum of **I.2a** at 77 K in 2-MeTHF (c). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is the UV-Vis absorption spectrum (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

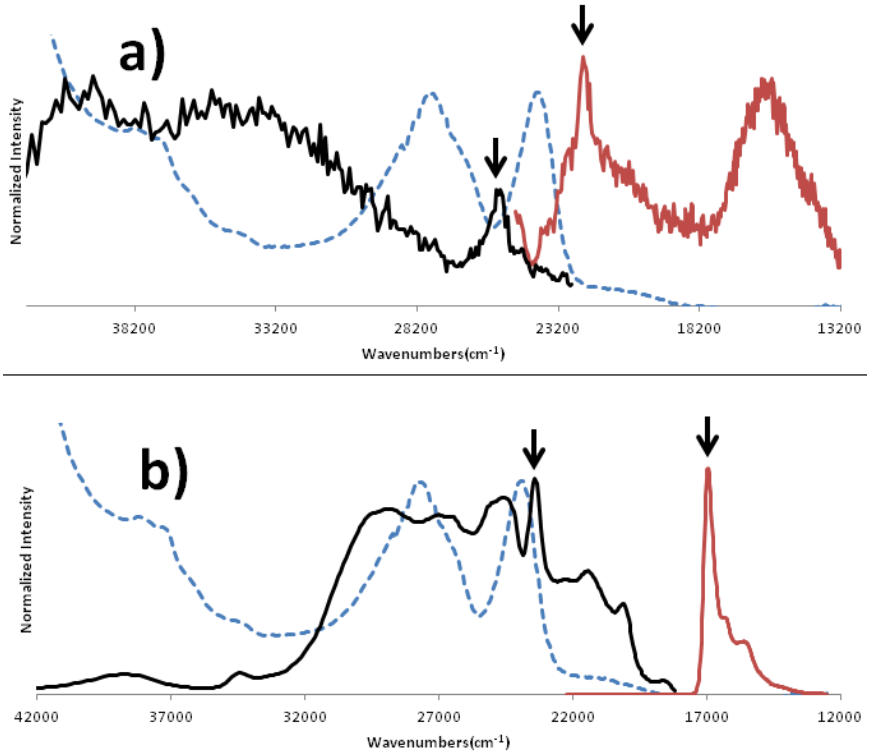


Figure 8: Fluorescence spectrum of **I.2c** at 293 K in CH_2Cl_2 (a). Phosphorescence spectrum of **I.2c** at 77 K in 2-MeTHF (b). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is the UV-Vis absorption spectrum (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

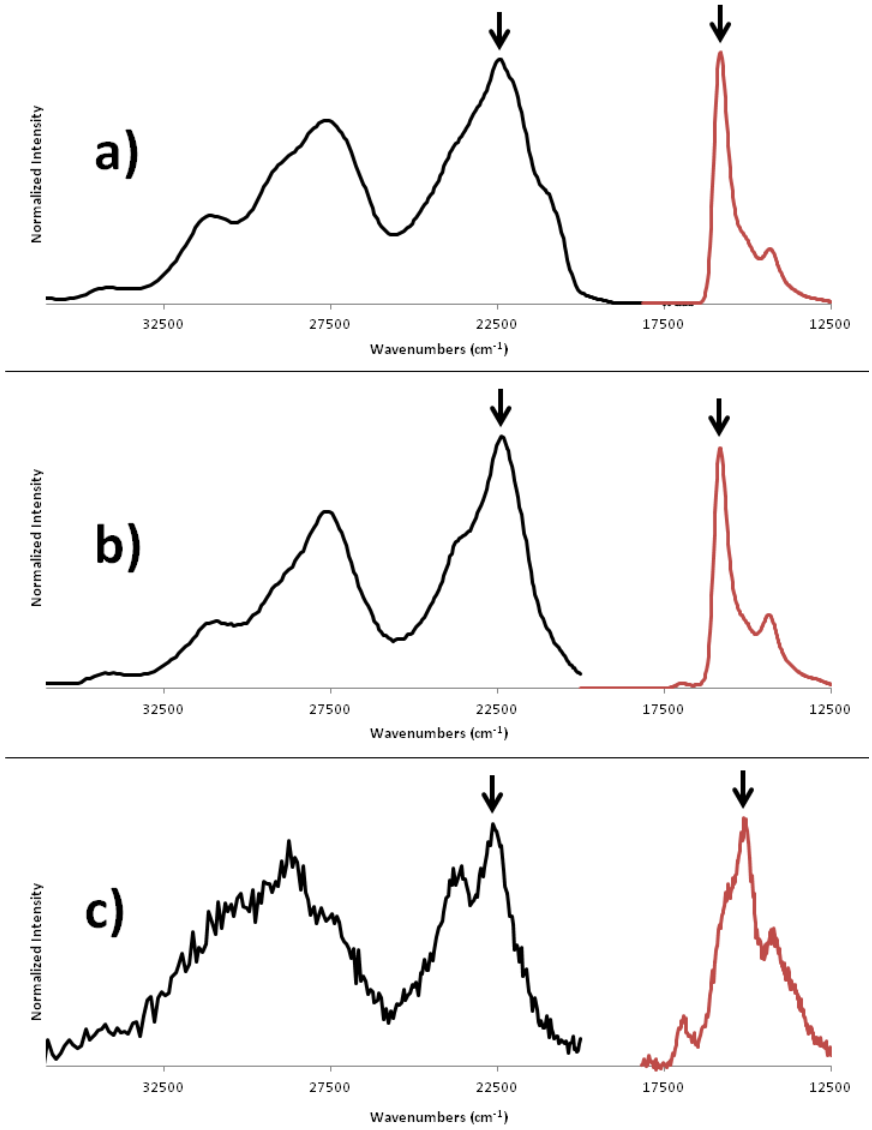


Figure 9: Phosphorescence spectra at 77 K in 2-MeTHF of (a) **I.2d**, (b) **I.2e**, and (c) **I.2f**. [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, black solid line is the excitation spectrum, red solid line is the emission spectrum]

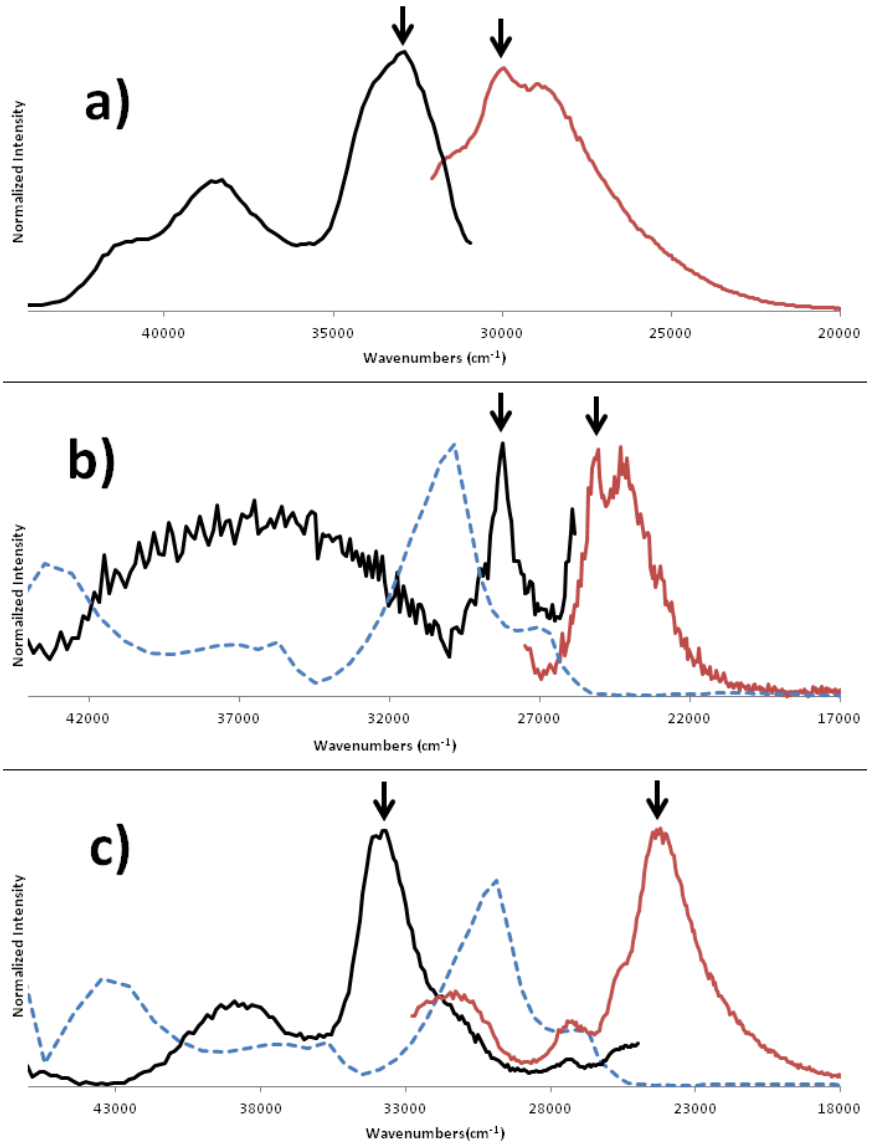


Figure 10: Fluorescence spectrum of residual BHT stabilizer at 293 K in 2-MeTHF (a). Fluorescence spectrum of **I.1c** at 293 K in CH_2Cl_2 (b). Fluorescence spectrum of **I.1c** at 293 K in 2-MeTHF with residual BHT stabilizer (c). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is the UV-Vis absorption spectrum of **I.1c** (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

X-Ray Diffraction Study of 2-thiolate-1,3-diethoxycarbonylazulene gold(I) triphenylphosphine (I.2a)

This study was conducted by Prof. Nikolay N. Gerasimchuk (Missouri State University - Springfield, MO). A clear light red-orange block-like specimen of $C_{34}H_{30}AuO_4PS$, approximate dimensions 0.070 mm x 0.080 mm x 0.110 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a triclinic unit cell yielded a total of 23,741 reflections to a maximum θ angle of 31.34° (0.68 Å resolution), of which 9,555 were independent (average redundancy 2.485, completeness = 97.9%, R_{int} = 2.98%) and 8,041 (84.15%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.7040(4) Å, b = 10.3830(5) Å, c = 16.6002(8) Å, α = 96.0340(10)°, β = 94.4100(10)°, γ = 90.2790(10)°, volume = 1,487.36(12) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The crystal has some appreciable absorption: μ=5.107 mm^{-1}

The final anisotropic full-matrix least-squares refinement on F^2 with 393 variables converged at R1 = 3.20%, for the observed data and wR2 = 6.00% for all data. The goodness-of-fit was 1.257. The largest peak in the final difference electron density synthesis was 1.680 $e^-/Å^3$ and the largest hole was -2.667 $e^-/Å^3$ with an RMS deviation of 0.219 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.703 g/cm^3 and F(000), 752 e^-.

X-Ray Diffraction Study of 6-thiolate-1,3-diethoxycarbonylazulene gold(I) triphenylphosphine (I.2c)

This study was conducted by Prof. Nikolay N. Gerasimchuk (Missouri State University - Springfield, MO). A clear light red-orange prism-like specimen of $C_{34}H_{30}AuO_4PS$, approximate

dimensions 0.075 mm x 0.080 mm x 0.090 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a triclinic unit cell yielded a total of 22,943 reflections to a maximum θ angle of 31.00° (0.69 Å resolution), of which 9,143 were independent (average redundancy 2.509, completeness = 98.4%, R_{int} = 3.85%) and 7,303 (79.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.8224(4) Å, b = 12.6279(5) Å, c = 14.0790(6) Å, α = 78.2800(10)°, β = 78.5020(10)°, γ = 73.7450(10)°, volume = 1,457.39(11) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(*I*).

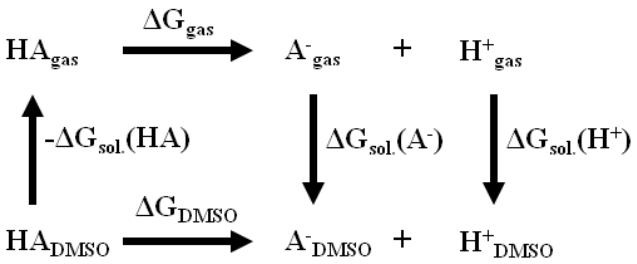
The final anisotropic full-matrix least-squares refinement on F^2 with 380 variables converged at R1 = 3.82%, for the observed data and wR2 = 7.67% for all data. The goodness-of-fit was 1.286. The largest peak in the final difference electron density synthesis was 2.086 $e^-/Å^3$ and the largest hole was -2.990 $e^-/Å^3$ with an RMS deviation of 0.271 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.738 g/cm^3 and F(000), 752 e^-.

Results and Discussion

Theoretical Predictions of pK_a Values in DMSO for Mercaptoazulenes

One of the first challenges was to determine the potential chemical reactivity involving the mercapto functionalities in the free ligands. As the acid / base chemistry can vary significantly depending on the electronics and sterics surrounding the aromatic ring, a quantitation of the acid dissociation constant (pK_a) of the mercaptans was desired. Numerous attempts at ascertaining the experimental pK_a's of various mercaptoazulenes were made according to the method employed by Brodwell, et al.[51] Due to experimental complications with

the procedure (e.g., precipitate formation and air-sensitivity), an alternative route was sought that employed density functional theory (DFT) considerations. Even if the absolute pK_a values were unattainable, the predictive value in relative pK_a measurements would still be of great interest. Because pK_a (in DMSO) is not a readily computed term, a thermodynamic cycle (see Scheme 6) was developed based upon the work of Shields, *et al*.[49]



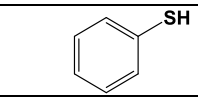
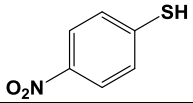
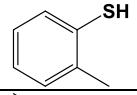
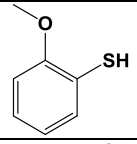
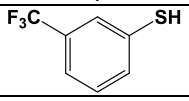
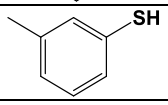
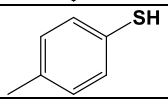
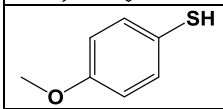
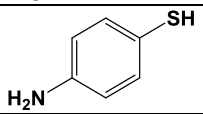
Scheme 6: Thermodynamic cycle used to calculate pK_a values for mercaptoarenes in DMSO based on the method of Shields, *et al*.[49]

While DFT can quite accurately determine the Gibb's free energies of acids and the corresponding conjugate bases, the situation with the proton, H^+, is more complex, as it has no electron density. To ascertain the combined free energy of the proton in gas phase and in DMSO, a series of established thiophenol derivatives[51] was used to back-calculate the free energy of the proton [$\Delta G_{gas+sol.}(H^+)$], see Equation 1 and Table 1. The average value for $\Delta G_{gas+sol.}(H^+)$ was then used to determine the 'Calculated pK_a' value to verify the model, see Equation 2. Figure 11 also shows the agreement between the calculated and experimental pk_a's.

$$\Delta G_{gas+sol.}(H^+) = -1.3644 * pKa_{Exp.} + \Delta G_{gas}(A^-) - \Delta G_{gas}(HA) + \Delta G_{sol.}(A^-) - \Delta G_{sol.}(HA) \quad (1)$$

$$pKa_{Calc.} = \frac{[\Delta G_{gas}(A^-) - \Delta G_{gas}(HA) + \Delta G_{sol.}(A^-) - \Delta G_{sol.}(HA) - \Delta G_{gas+sol.}(H^+)]}{1.3644} \quad (2)$$

Table 1: The series of thiophenols used in the determination of the $\Delta G_{gas+sol.}(H^+)$ value. The calculated pK_a was then compared to the experimental pK_a[51] with error analysis. See also Tables A1.18 – A1.35 & A1.60.

Compound	$\Delta G_{gas+sol.}(H^+)$	Experimental pK_a	Calculated pK_a	$\lvert pk_a(exp.) - pk_a(calc.) \rvert$
	274.02	10.28	10.31	0.03
	272.73	5.50	4.58	0.92
	274.00	10.70	10.71	0.01
	274.84	11.35	11.97	0.62
	273.85	8.09	7.99	0.10
	273.49	10.55	10.19	0.36
	274.07	10.82	10.88	0.06
	274.82	11.19	11.80	0.61
	274.07	12.51	12.57	0.06
Average	**273.99**			**0.31**
Std. Dev.	**0.64**			**0.34**

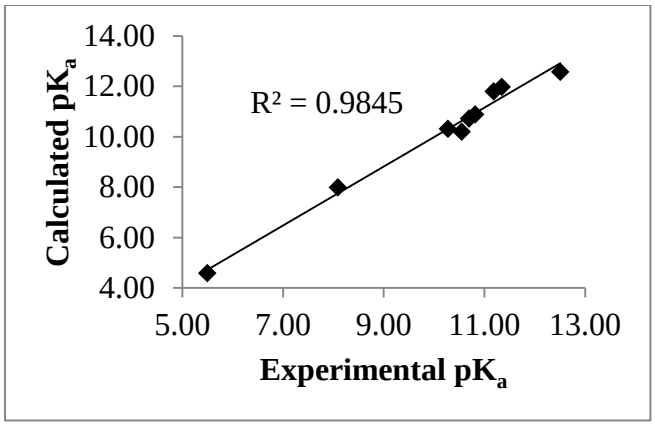


Figure 11: A linear plot showing the agreement between the calculated and experimental pK_a values for the series of thiophenols listed in Table 1.

After achieving a reasonable model to ascertain the pK_a's of various mercaptoarenes in DMSO, the currently unknown experimental pK_a's of many mercaptoazulene derivatives were determined using Equation 2, see Figure 12. In an effort to reduce the computational cost, the ethoxycarbonyl groups were truncated to methoxycarbonyl groups, and the triphenylphosphine (PPh_3) ligand was truncated to trimethylphosphine (PMe_3). These truncations should not significantly impact the electronic environment of the –SH group.

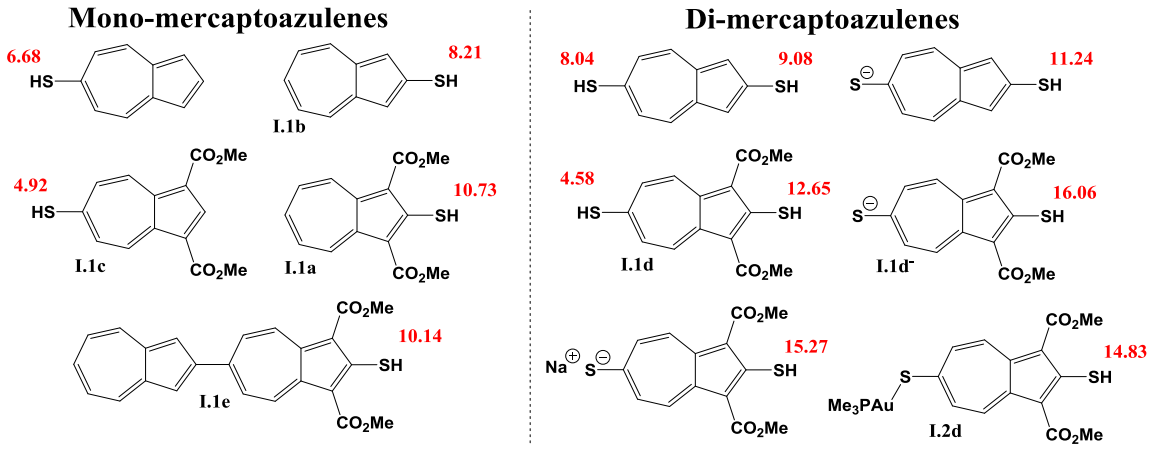


Figure 12: Theoretical pK_a's (in red) of various mono- (left) and di- (right) mercaptoazulenes in DMSO ±0.31 pK_a units. Also, see Tables A1.36 – A1.58 and A1.61.

Very interesting trends appeared to emerge from the theoretical pK_a determinations of the mercaptoazulenes. It is clear that a simple comparison of isomers, *i.e.* **I.1a** and **I.1c**, of the mono-mercaptoazulenes (Figure 12, left) shows a change in pK_a between 2 to 6 units. This distinction between 6-mercapto- and 2-mercaptoazulenes carries over to the 2,6-dimercaptoazulene systems (Figure 12, right). When no methoxycarbonyl groups are present in the dimercaptoazulenes, there is only a 1 pk_a unit difference between the 2- and 6-mercapto termini. This difference jumps to 8 pk_a units due to the stereoelectronic influence of the methoxycarbonyl groups in **I.1d**. The staggering separation in acidities between mercapto termini allows for the remarkable regioselectivity observed in the synthesis of **I.2d** and **I.2e**, shown in Scheme 1.[4] Also investigated was the 2-SH terminus pK_a as the 6-terminus is changed from a simple thiolate anion (**I.1d**$^-$), to a sodium-thiolate ion pair, and to a bound gold(I) phosphine (**I.2d**). The 2-SH terminus shows relatively similar values for all three systems with a change of only 1.7 pK_a units between them.

Gold(I) Complexes of Mercaptoazulenes

In order to build a library of mercapto-azulene gold(I) complexes based on the Barybin Group's initial studies of **I.2d** and **I.2e**[4], a series of mono-mercaptoazulenes **I.1a-c, I.1e** was selected for complexation. Just as the pK_a studies suggest (*vide supra*), a strong base (NaOMe) was needed to deprotonate the terminal –SH group in the cases where the conjugate base is of higher energy due to the unfavorable electrostatic interactions with the neighboring ethoxycarbonyl groups, see **I.1a, I.1f**. In cases without such unfavorable electrostatic interactions, lower strength bases, such as NEt_3 can be used; however, the use of NaOMe is preferred in all cases as it offers the advantage of simplified product purification steps.

Upon isolation of the complexes **I.2a** and **I.2c**, X-ray quality crystals of each were grown via slow solvent diffusion to form needles. The Oak Ridge Thermal Ellipsoid Plot (ORTEP)[52] drawings for these structures are shown in Figures 13 and 14, respectively. While the ethoxycarbonyl groups tend to be disordered, their crystallographic disorder was successfully modeled. Of remarkable interest is the highly strained structure of **I.2a** that features the average torsion angle of the carbonyl groups relative to the azulene plane of 90.8°. This falls in line with the DFT predicted significant torsional strain associated with this motif.[4] Additionally, the P-Au-S bond angle of 173.70(3)° bent away from the azulenylthiolate unit is statistically different (using the 3σ criterion) from the corresponding more linear angles documented for **I.2d** [178.56(6) and 176.20(6)º].[4]

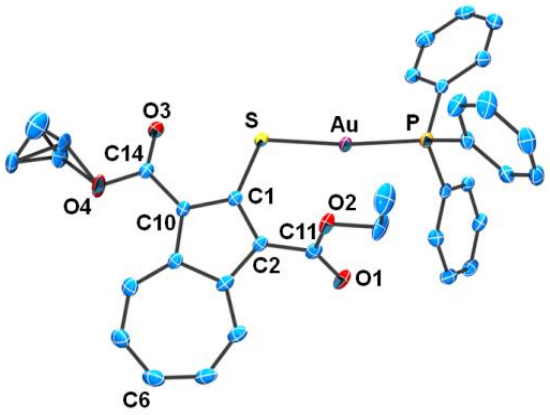


Figure 13: X-ray crystal structure of **I.2a** generated using ORTEP. Ellipsoids drawn at 50% probability, and all hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Au-P 2.2690(9), Au-S 2.3006(9), S-C1 1.745(3), P-Au-S 173.70(3), Au-S-C1 111.71(11), O1-C11-C2-C1 -127.8(4), O2-C11-C2-C1 56.2(4), O3-C14-C10-C1 9.1(5), O3-C14-C10-C1 -170.1(3).

In contrast to the strain observed in the structure of **I.2a**, its isomer **I.2c** shows a more typical conformation of the carbonyl groups, where they are locked in the azulene plane with the carbonyl oxygen atoms pointed towards the seven-membered ring, presumably, via a weak

intramolecular hydrogen bond[53], see Figure 14. One other point is the unusually short contact between the hydrogen stemming from a meta-position in the PPh_3 system and an ester carbonyl group. In this case, the P-Au-S bond angle of 168.49(4)° is bent towards the carbonyl group of the azulenylthiolate moiety, which is also statistically significant (using the 3σ criterion). This short contact also likely involves a weak intramolecular hydrogen bond as the C(phenyl) – O1 distance is 3.485 Å and C(phenyl)-H34-O1 bond angle is 168.03°.[53]

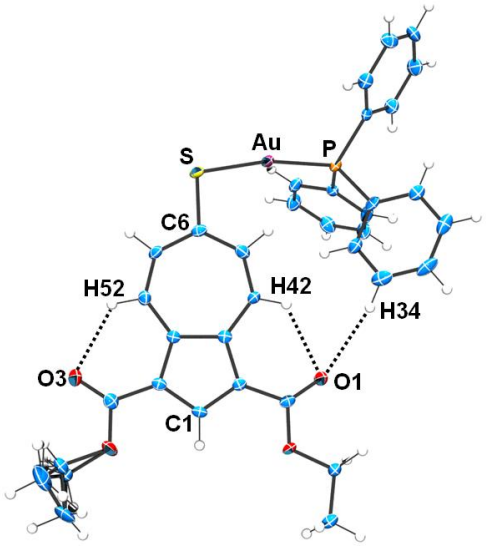


Figure 14: X-ray crystal structure of **I.2c** generated using ORTEP. Ellipsoids drawn at 50% probability, and dashed lines indicate short intramolecular contacts. Selected bond distances (Å) and angles (°): Au-P 2.2538(11), Au-S 2.3208(12), S-C6 1.762(4), P-Au-S 168.49(4), Au-S-C6 103.30(15), O1···H34 2.574, O1···H42 2.390, O3···H52 2.377.

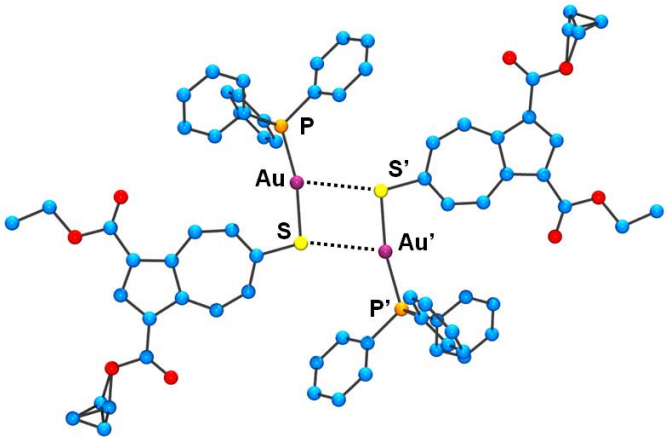


Figure 15: Ball and stick model of the X-ray crystal structure of **I.2c** generated using ORTEP showing intermolecular contacts (dashed lines). All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Au-Au' 4.250, S-S' 3.599, Au-S' 3.181, Au-S-Au' 99.96, S-Au-S' 80.04, Au-S-Au'-S' 0.00.

The packing diagram for **I.2c** is quite intriguing as it features a four-membered metallocycle involving the gold(I) and sulfur atoms of two molecules, see Figure 15. This is a more typical structural motif in gold(I) thiolate phosphines when steric hindrances (such as those in **I.2a**) do not preclude the formation of larger supramolecular structures.[23] While the gold(I) – gold(I) distance of 4.250 Å does not indicate presence of any aurophilic interactions, the four-membered ring is still a planar system.

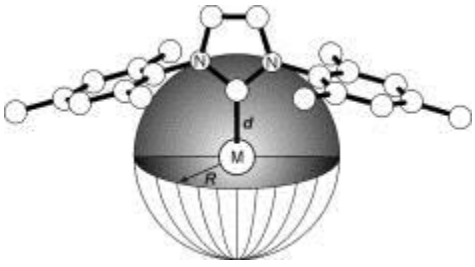


Figure 16: Example showing how the buried volume (%V_{Bur}) is calculated, where M is the metal center, d is the distance (in Å) between the metal and ligand, and R is the radius (in Å) of the sphere.[54] [Figure reprinted with permission, Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]

To probe the extent of steric hindrance around the gold(I) center exerted by the 2- vs 6-azulenylthiolate coordination in complexes **I.2a** and **I.2c**, respectively, the atomic coordinates of the crystal structures were submitted to the Samb*V*ca web application[54] for determining the percent buried volume (%V_{Bur}). Much akin to the Tolman cone angles[55,56], the %V_{Bur} allows for the quantitation of the sterics surrounding the metal center. The %V_{Bur} is calculated by the percent volume taken up by the ligand in a sphere with the metal placed at the center, see Figure 16. With the sphere radius (R) at 3.5 Å, distance from the metal center (d) at 2.3 Å, mesh spacing at 0.05 Å, bond radii scaled by 1.17, and hydrogen atoms being omitted, the %V_{Bur} for the azulenylthiolates are 32.5% for **I.2a** and 17.6% for **I.2c**. Based on the %V_{Bur} analysis, the ethoxycarbonyl groups cause nearly double the amount of steric hindrance surrounding the gold(I) center on **I.2a** vs. **I.2c**.

Solution Phase Dynamics addressed by NMR Methods

Given the rather busy ^{1}H and ^{13}C NMR patterns for complexes **I.2a-f**, ^{31}P NMR has proven to be a simple means to determine formation of these products. Table 2 compares the ^{31}P NMR chemical shifts documented for complexes **I.2a-f**. When ethoxycarbonyl groups at 1,3-positions of the azulenic framework are sterically hindering the gold(I) thiolate phosphine moiety, the ^{31}P{^{1}H} NMR resonance occurs at *ca.* 36.4 ppm, as observed for **I.2a**, **I.2e** (on the 2-thiolate terminus), and **I.2f**. When no significant steric hindrance is present, $\delta(^{31}P)$ is *ca.* 38.0 ppm regardless of the position of attachment of the azulenic scaffold to the thiolate junction, which is in line with the $\delta(^{31}P)$ values documented for other gold(I) phosphine aryl thiolate complexes (39.2 ppm).[57,58] One potential issue with using NMR as a characterization technique is its relatively long timescale resulting in the possibility of signal averaging due to a fast dynamic process. Solutions of complex **I.2e**, indeed, shows a rapid exchange of the two ^{31}P

environments on the NMR timescale that was resolved through variable temperature NMR studies.[4]

Table 2: Comparison of $^{31}P\{^{1}H\}$ NMR chemical shifts (vs. 85% aqueous H_3PO_4) for complexes **I.2a-f** in $CDCl_3$ or CD_2Cl_2 at *ca.* 24 °C. *Recorded at -40 °C

Complex	**^{31}P NMR Shift (ppm)**
I.2a	36.49
I.2b	38.34
I.2c	37.98
I.2d	37.89
I.2e	37.95*, 36.19*
I.2f	36.41

To further probe the exchange processes at play, ^{31}P NMR was again used to monitor the equilibrium between **I.2a** and an added equivalent of PPh_3, see Figure 17. Figure 17b shows the signal averaged peak indicating a rapid equilibrium relative to the NMR timescale. In hopes of slowing down the forward and reverse reaction rates to observe discrete ^{31}P resonances for coordinated and free PPh_3 ligands, the sample from Figure 16b was subjected to variable temperature $^{31}P\{^{1}H\}$ NMR analysis, see Figure 17. Upon cooling the sample, the ^{31}P peak at 15.61 ppm gradually diminished in intensity to ultimately disappear into the baseline. This indicates two scenarios: 1) the coalescence point has been reached at *ca.* -75 ºC; 2) the solute(s) in the sample precipitated out of solution to a large extent. In the case of the former, this would suggest a very rapid exchange process occurring. Without being able to clearly observe new arising peaks in the lower temperature NMR spectra, it is difficult to draw unambiguous conclusions.

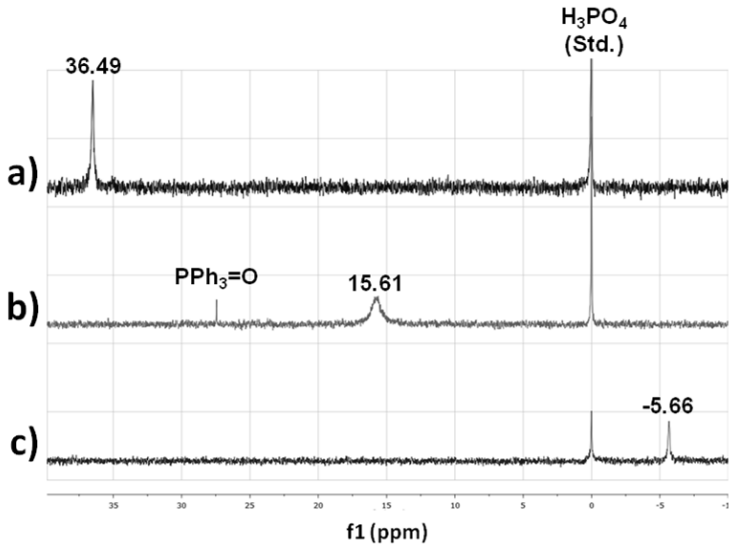


Figure 17: $^{31}P\{^{1}H\}$ NMR spectra (202 MHz, $CDCl_3$, 22 °C, 85% aq. H_3PO_4 externally referenced) of (a) **I.2a**, (b) **I.2a** + 1 eq. PPh_3, and (c) PPh_3.

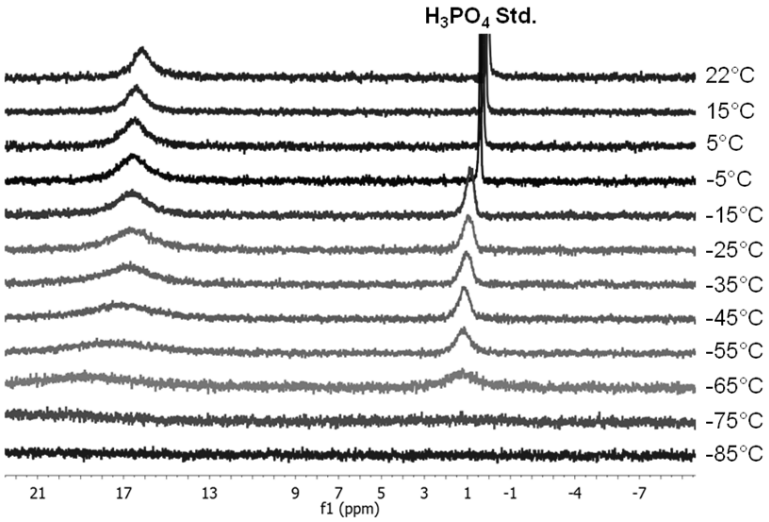


Figure 18: Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **I.2a** + 1 eq. PPh_3 in $CDCl_3$.

A solution of **I.2b** containing *ca*. 1 eq. of $Et_3NH^+Cl^-$ from the synthesis using Et_3N as the base (instead of NaOMe), was subject to Diffusion Ordered Spectroscopy (DOSY) NMR analysis, see Figure 19. DOSY NMR is a 2D technique that correlates ^{1}H NMR resonances (x-axis) with the corresponding diffusion coefficients of each ^{1}H NMR environment along the y-

axis. Sometimes referred to as 'NMR chromatography', DOSY NMR can help resolve multiple species in solution by separating them based on differences in their diffusion properties. The DOSY NMR spectrum in Figure 19 clearly shows that the Et_3NH^+ cation has diffusion characteristics similar to those of the azulenylthiolate gold complex (**I.2b**). Because **I.2b** and $Et_3NH^+Cl^-$ independently are expected to have very different diffusion coefficients based on their substantially different molecular volumes, the almost identical diffusion coefficients suggested by the DOSY NMR indicate that these species are associated in solution, likely through an equilibrium reaction summarized in Scheme 7.[59]

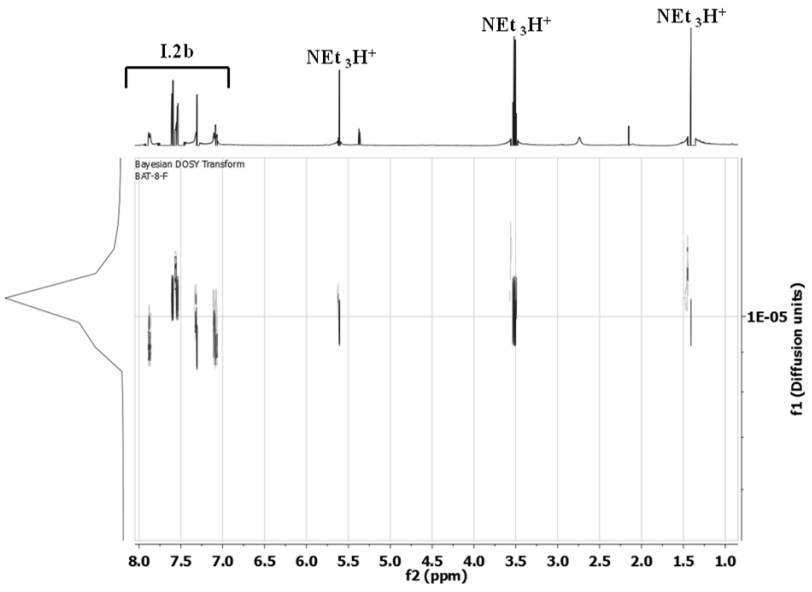
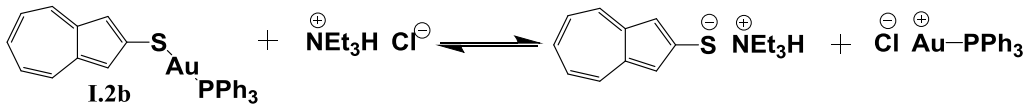


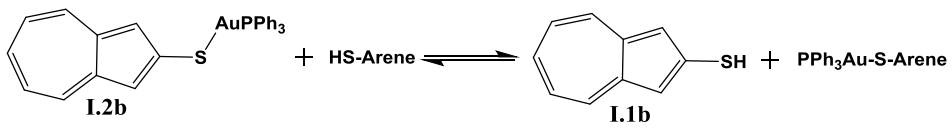
Figure 19: Diffusion Ordered Spectroscopy (DOSY) NMR of **I.2b** with *ca.* 1 eq. of $NEt_3H^+Cl^-$ in CD_2Cl_2 at 24.4 °C on a 500 MHz NMR.



Scheme 7: Proposed equilibrium reaction between **I.2b** and $Et_3NH^+Cl^-$.

Reactivity Studies of Gold(I) Complexes

While the theoretical determinations of pK_a (DMSO) for the mercapto-azulenes **I.1a-e** are compelling, their predictive value needed to be put to the test. An experiment was devised based upon the extensive evidence of the gold(I) – thiolate bond scission in ambient solutions. The experiment, shown in Scheme 8, would take an already isolated gold(I) complex (**I.2b** in this instance) and add an equivalent of some mercaptoarene. The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were acquired and monitored for the resulting product versus reactant distribution. Specifically, the ratio of integrated peak intensities corresponding to the –SH groups was used to determine the equilibrium constant (K), which was then used to determine the Gibb's free energy (ΔG) of the reaction, see Table 3. As the predicted pK_a (DMSO) of the free ligand **I.1b** is 8.21 units, the reactions of I.2b with mercaptoarenes having lower pK_a, such as **I.1c**, should proceed in the forward direction (*i.e.* $\Delta G < 0$), while its reactions with less acidic mercaptoarenes would be unfavored (*i.e.*, $\Delta G > 0$). While differences in the bond disassociation energy (BDE) of the Au-S bonds may impact the observed equilibrium, the typical Au-S bond length in gold(I) phosphine thiolate crystal structures is *ca.* 2.3 Å, with very minor deviation.[58,60] As the BDE can be correlated to the bond length, the observed equilibrium should not be greatly impacted by the variations in Au-S BDE.[61] All predictions based on the theoretical pK_a's were indeed in accordance with the experimentally observed reactivity outcomes. Because the ^{31}P NMR resonances of all of the major gold(I) complexes in solution are essentially identical for Table 3, no significant shifts in the resonances were detected.



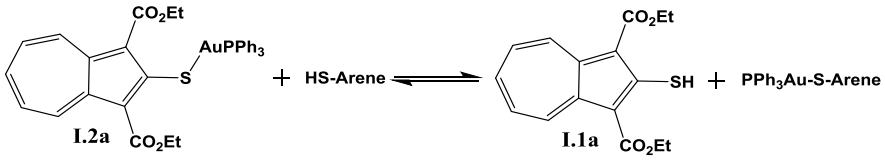
Scheme 8: Reaction between **I.2b** and various mercaptoarenes, see Table 3.

Table 3: NMR reactivity studies based on addition of *ca.* 1 eq. of a mercaptoarene to **I.2b**, see Scheme 8.

*Theoretically predicted values.

HS-Arene	pK_a (DMSO)	K_{eq}	ΔG (kcal / mol)
I.1a	10.73*	0.029	+2.06
I.1c	4.92*	10.14	-1.36
Thiophenol	10.28	0.12	+1.24

A similar set of experiments was performed for complex **I.2a** (see Scheme 9). The theoretical pK_a (DMSO) of the corresponding free mercaptoazulene, **I.1a**, is 10.73. In all cases, the reaction proceeded essentially to completion forming a new gold(I) complex that featured the incoming aryl thiolate ligand, as validated by the corresponding positive shift of the ^{31}P NMR resonance (see Table 4). Again, this series of results indicates excellent qualitative agreement between the theoretical models and experimental observations concerning pK_a's of the mercaptoazulenes.



Scheme 9: Reaction between **I.2a** and various mercaptoarenes, see Table 4.

Table 4: NMR reactivity studies based on addition of *ca.* 1 eq. of mercaptoarene to **I.2a**, see Scheme 9.

*Theoretically predicted values.

HS-Arene	pK_a (DMSO)	K_{eq}	ΔG (kcal / mol)	$\Delta^{31}P$ Shift (ppm)
I.1b	8.21*	866.31	-4.00	+1.84
I.1c	4.92*	10.01	-1.36	+1.95
Thiophenol	10.28	35.83	-2.11	+2.14

Photoluminescence Measurements of Ligands and Complexes

Due to the storied history of azulene and its derivatives as the classic 'rule breakers' to Kasha's Rule, explorations into the photophysics of the mercaptoazulenes and their gold(I) complexes were undertaken. Observations at both room temperature (293 K) and 77 K pointed to some rather interesting findings, as summarized in Figures 4 – 8 on pages 13-19 and Table 5. The origin of the photon emission can be qualitatively determined by overlaying the electronic absorption spectrum with the fluorescence excitation and emission spectra. By matching the maximum excitation ($\lambda_{Ex.}$) with an absorption band in the electronic spectrum, the originating state can be assigned to the emission. This approach to emissive state assignment can be difficult to interpret and more definitive results can be obtained by examining the excitation spectrum at 4 K using a frozen argon matrix, which was not an experimentally accessible in this work. The free ligands based on the 2-mercapto-1,3-diethoxycarbonylazulene motif (**I.1a** and **I.1d**) showed nearly identical photophysical behavior. In both cases, the emission correlates with originating from the S_1 state, which means Kasha's Rule is respected. More interesting though is that **I.1c**, which is an isomer of **I.1a**, seems to be emitting from the S_2 state, in contradiction to Kasha's Rule. This trend continues when looking at the corresponding gold(I) phosphine complexes, **I.2a** and **I.2c**. To help shed light on this discrepancy, DFT was employed to determine the orbital diagrams of the frontier molecular orbitals for the truncated models of **I.1a**, **I.1c**, and **I.1d**, see Figure 20, and **I.2a** and **I.2c**, see Figure 21.

The DFT computed frontier molecular orbitals of the mercaptoazulenes **I.1a** and **I.1c**, shown in Figure 20, reveal that there is an apparent switch between the HOMO and HOMO-1. In **I.1a**, the HOMO-1 is primarily an azulene centered π system, and the HOMO of the system involves part of the azulene π system with a large contribution from the lone pairs of the

mercapto functionality. With the isomer **I.1c**, the energy order of these orbitals is reversed. This switching in the ground state could have implications for the excitations into the S_1 and S_2 states. If the photophysical excitations are different for **I.1a** and **I.1c**, then this could give rise to a change in the fluorescence emissive states. Also of note is the large difference in orbital densities between isomeric complexes **I.2a** and **I.2c**. While the orbital density suggests that all transitions in the frontier area are azulenyl thiolate-based [intra-ligand charge transfers (ILCT)], how that density is distributed varies greatly, akin to the corresponding free mercaptoazulene ligands.

Table 5: Fluorescence excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) data.

Compound	**Conditions**		**Fluorescence**		
	Solvent	**Temperature (K)**	**$\lambda_{Ex.}$(cm^{-1})**	**$\lambda_{Em.}$(cm^{-1})**	**Stokes Shift (cm^{-1})**
I.1a	CH_2Cl_2	293	24691	23529	1162
	2-MeTHF	77	23362	21276	2086
I.1c	CH_2Cl_2	293	28248	25067	3181
I.1d	CH_2Cl_2	293	21096	19922	1174
	2-MeTHF	77	21096	18215	2881
I.2a	CH_2Cl_2	293	23921	23148	773
	2-MeTHF	77	24572	21690	2882
I.2c	CH_2Cl_2	293	25252	22327	2925

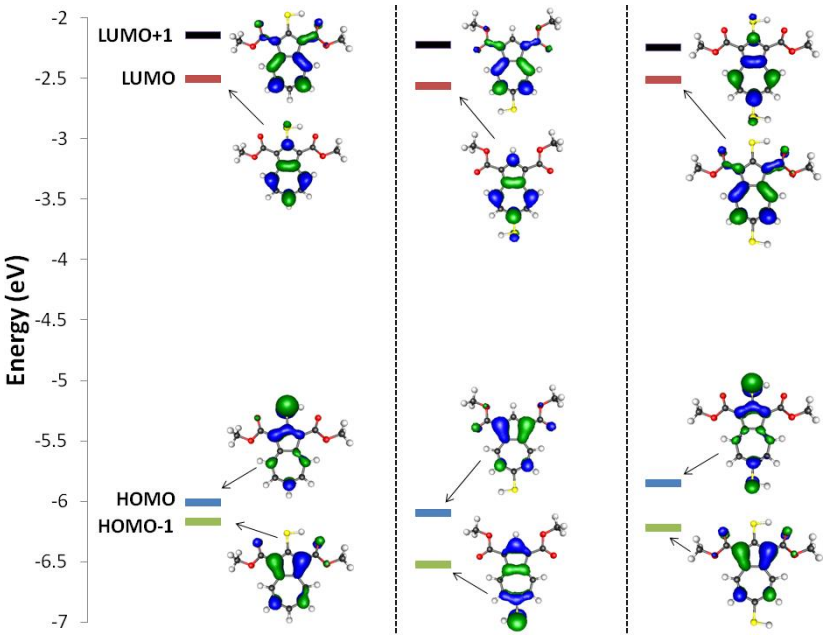


Figure 20: Frontier molecular orbitals calculated using DFT (Opt & SP B3LYP/TZVP) for truncated models of **I.1a** (left), **I.1c** (center), **I.1d** (right).

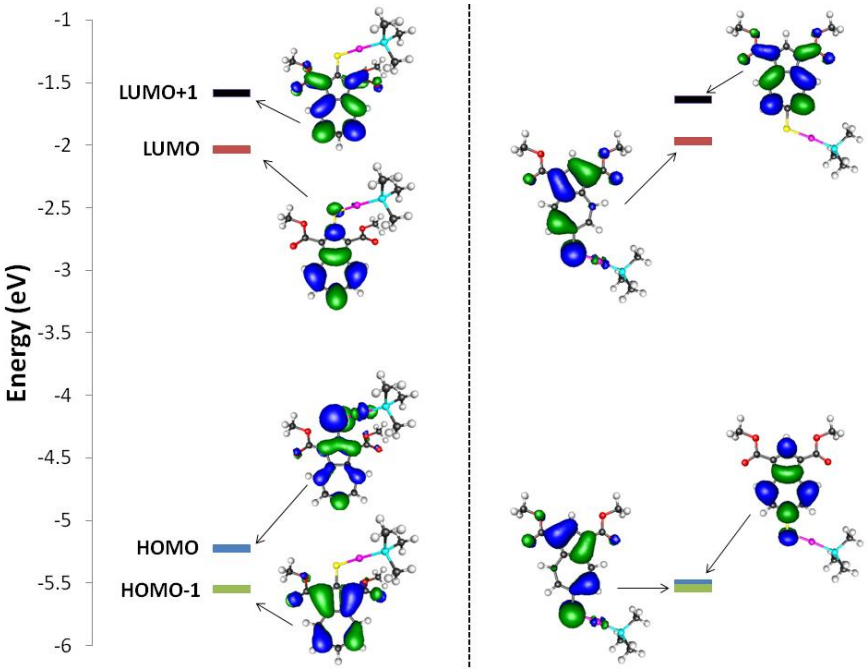


Figure 21: Frontier molecular orbitals calculated using DFT (Opt: BP86/TZVP & SP: B3LYP/TZVP) for truncated models of **I.2a** (left), **I.2c** (right).

One reason low temperature studies were undertaken in the first place was to observe any phosphorescence from the various mercaptoazulene derivatives and their complexes. Typically, organic molecules are most likely to show phosphorescent behavior in frozen solutions due to the inability to vibrationally relax via interactions with the solvent. The collected data (Figures 4c, 5b, 6c, 7c, 8b, 9, and Table 6) show fairly consistent behavior across all systems studied. In all cases, there is an absorption into the S_1 which then, via an intersystem crossing, proceeds to a triplet state (most likely the T_1).[15] The triplet state relaxes back down to the ground state (S_0) with the corresponding emission observed at *ca.* 616 nm (16230 cm^{-1}), and in many cases some vibronic structure is evident. Additionally, lifetimes of the phosphorescent states were measured with an average lifetime of 5.6 ms.

Table 6: Phosphorescence excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) data collected in 2-MeTHF at 77 K.

Compound	**Phosphorescence**			
	$\lambda_{Ex.}$(cm^{-1})	**$\lambda_{Em.}$(cm^{-1})**	**Stokes Shift (cm^{-1})**	**Lifetime (ms)**
I.1a	22672	16695	5977	2.413 ± 0.2
I.1c	23255	16890	6365	21.412 ± 1.3
I.1d	20704	15551	5153	4.773 ± 0.3
I.2a	23809	16978	6831	3.400 ± 0.0
I.2c	23421	16949	6472	3.569 ± 0.0
I.2d	22471	15823	6648	3.777 ± 0.0
I.2e	22418	15848	6570	3.899 ± 0.0
I.2f	22626	15106	7520	1.585 ± 0.1

As a cautionary tale, a researcher should always take care to ensure the quality of solvents used in spectroscopic experiments. Butylated hydroxytoluene (BHT) was a known stabilizer in 2-methyltetrahydrofuran (2-MeTHF). This solvent was needed to form a glass at low temperatures. When the initial studies were conducted, a fluorescence spectrum of the pure solvent was obtained, see Figure 10a. While there was a significant fluorescence pattern

observed due to the BHT, it was seen only at higher energies (λ_{Ex} = 300 nm and λ_{Em} = 330 nm). Because the key absorption bands in the electronic spectra of the mercaptoazulene derivatives were much lower in energy, the stabilizer was deemed not likely to impact the fluorescence of the azulenic compounds in question. However, a curious feature was noted in the spectrum of **I.1c** in 2-MeTHF. Despite precedence for azulene derivatives to break Kasha's Rule (condensed phase fluorescence from greater than the S_1 state), compound **I.1c** appeared to be fluorescing from greater than the S_3 state. This feature was quite troubling additionally due to the fact that there was almost no absorption detected in the electronic spectrum that correlated with the fluorescing state (see Figure 10c). After many trials and tribulations, it was eventually documented that the same room temperature fluorescence spectra of **I.1c** in CH_2Cl_2 showed a significantly different pattern that fit the electronic absorption spectrum data with emission, see Figure 10b. What appears to be happening is that there is the formation of an excited dimer (termed excimer) in solution between the BHT stabilizer and **I.1c**. This excimer works, as shown in Figure 22, by exciting to the S_1 state of BHT at 296 nm. The emission from BHT then occurs at 330 nm, which correlates to a large absorption feature in the electronic spectrum of **I.1c**. Subsequent excitation of, **I.1c** leads to fluorescence emanating at 412 nm with a lifetime of 30 ps [T. Quincy & C. G. Elles (University of Kansas), Unpublished]. Given that the concentration of BHT in solution is between 6.8 x 10^{-4} and 1.8 x 10^{-3} mol / L, there is a substantial amount of BHT present that can lead to the excimeric fluorescence pattern. One last point is that **I.1a**, which is an isomer of **I.1c**, exhibited no such energy transfer processes and had nearly identical fluorescence patterns recorded for its solutions in both CH_2Cl_2 and 2-MeTHF. A possible explanation for the different behavior of the isomers is the change in emissive states for **I.1a** and **I.1c**, *vide supra*.

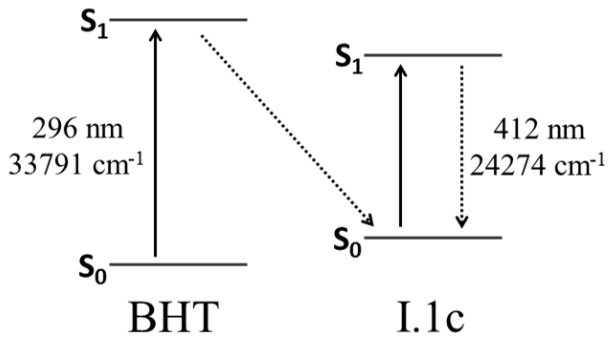


Figure 22: A simplified Jablonski diagram accounting for the excimeric interaction between butylated hydroxytoluene (BHT) and **I.1c**.

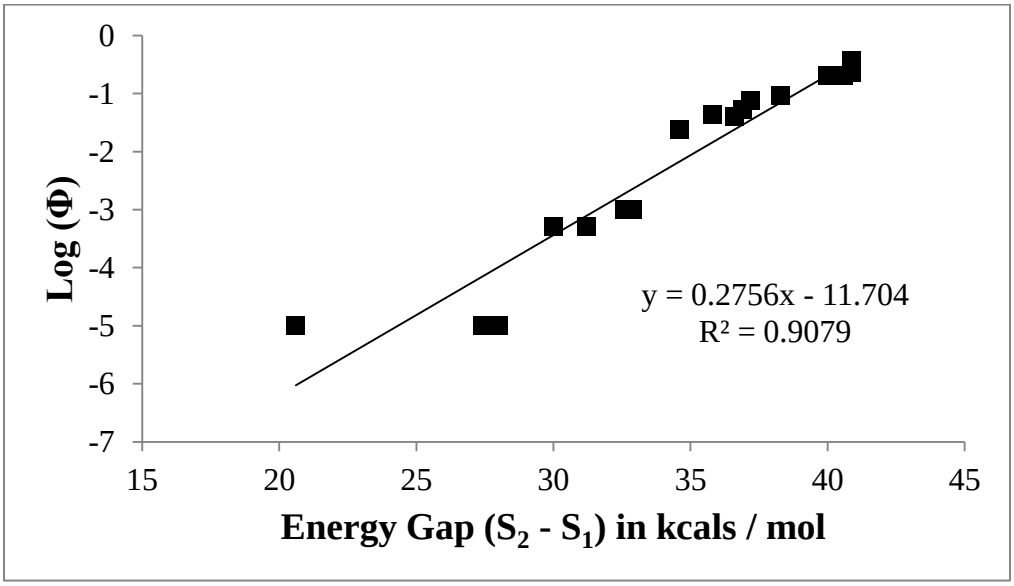


Figure 23: An energy gap law plot for azulene derivatives. Data for the plot were taken from ref 62. (Φ = fluorescence quantum yield)

Much work in the literature has related the energy gap between the S_2 and S_1 states of azulene derivatives to their fluorescence quantum yield (termed "the energy gap law").[63,64] Based on the above plot (Figure 23), many azulene derivatives follow the energy gap law relating the energy separation between the S_2 and S_1 states (primarily relating to the LUMO+1 and LUMO orbitals, respectively) and the experimentally determined quantum yield (Φ) of the

system.[62] Some noted exceptions to the trend are due to the introduction of a non-bonding orbital in the ground state, as found for formyl-substituted azulenes.[18,65] Given the possibly different fluorescence nature between **I.1a** and **I.1c**, it will be interesting to see if the energy gap law, illustrated in Figure 23, holds true. Further studies of the fluorescence quantum yield and lifetime measurements will be crucial in assigning the emission from either the S_1 or S_2 states for all systems.

Conclusion and Future Work

The synthesis and structural characterization of novel gold(I) phosphine azulenylthiolate complexes was described. Through extensive use of NMR methods, the reactivity dynamics of these systems was explored. Theoretical determinations of the acid disassociation constants of the free mercaptoazulene ligands were corroborated by systematic reactivity studies involving the new gold(I) azulenylthiolate complexes. The first photoluminescence studies of the mercaptoazulene ligands and the corresponding gold(I) complexes suggest unusual switching of the emissive state, S_1 for **I.1a** and S_2 for **I.1c**, between the isomeric pairs.

Obtaining satisfactory elemental analyses for the gold(I) complexes reported herein will be necessary to prove their purity in bulk. X-ray quality crystals will also be targeted for both **I.2b** and **I.2f**. Completion of the photoluminescence measurements on the family of both ligands and complexes will involve quantum yield and lifetime determinations.

The mercaptoazulenic species, as well as complexes thereof with monovalent gold, have been designed as a part of the Barybin group's long-term quest for azulene-based molecular rectifiers. While the availability of mercaptoazulenes and their organometallic variants may ultimately lead to significant breakthroughs in molecular electronics, the photoluminescent

behavior of these systems, which has been partially unraveled through the work described in this Chapter, is of great fundamental interest as well. These compounds constitute attractive platforms for developing new, relatively non-toxic, photoluminescent materials for possible applications in optical sensing. Of particular importance will be the possibility of achieving emission from multiple excited states for some of these materials, which may pave the way for designing azulenic ratiometric optical sensors in the future.

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CHAPTER 2

Efficient synthesis and completely regioselective metallation of the 2,6-dimercatoazulene motif: A synergistic synthetic, spectroscopic and computational study

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This Chapter is based on the work recently published in

Chemical Science, **2013**, *4*, 4267-4272.

Abstract

In the past few years, several theoretical studies predicted that the hypothetical 2,6-dimercaptoazulene framework should behave as a highly conductive molecular rectifier.[1-3] This Chapter details the design and two efficient synthetic routes to the first 2,6-dimercaptoazulene derivative, which is an extremely rare example of an unsymmetric dimercaptoarene, as well as successive formation of its mono- and dinuclear complexes with Au(I). The two SH termini in the 2,6-dimercapto-1,3-diethoxycarbonylazulene linker exhibit profoundly different acidities, which permits completely regioselective metallation of its 6-SH terminus. The origin of this remarkably regioselective complexation was addressed via a systematic density functional theory analysis. The dinuclear Ph_3PAu^I complex featuring the 2,6-azulene dithiolate bridge undergoes rapid exchange of its ^{31}P NMR environments at ambient temperature, which was attributed to reversible S-Au rather than Au-P bond scissions. This system serves as a unique unsymmetric platform to observe the exchange of gold-bound thiolates by employing a single compound.

Introduction

The quest for implementation of the principles that govern the design of molecular conductors and rectifiers has led to theoretical and experimental interest in linear dimercaptoarenes, such as 1,4-dimercaptobenzene (Figure 1, left).[4-6] The key structural feature of a good molecular conductor (or a single-molecule wire) is a conjugated planar π-framework that supports charge transfer between the donor and acceptor termini.[7] While the vast majority of systems considered in this regard incorporate benzenoid π-linkers, theoretical analysis of a scaffold composed of fused sp^2-carbon pentagons and heptagons may rival metallic conductivity.[8] Azulene, a nonbenzenoid bicyclic aromatic hydrocarbon featuring a pair of fused

five- and seven-membered sp^2-carbon rings, represents the smallest unit of this type. The azulenic motif has a dipole of about 1.1 Debye[9] along its molecular axis, so 2,6-functionalized azulenes essentially behave as molecular diodes. Several theoretical studies[1-3] specifically looked at the hitherto unknown 2,6-dimercaptoazulene framework and concluded that it would be a very attractive linker for supporting charge delocalization and transfer, especially compared to its benzenoid isomer, 2,6-dimercaptonaphthalene, for which conductivity characteristics have been recently assessed experimentally, see Figure 1.[10,11] Since neither 2,6-dimercaptoazulene nor any of its derivatives had been described in the literature, the Barybin Group endeavored to fill this void, turning first to the chemistry of mono-mercaptoazulenes that has remained dormant for decades and then employing azulenyl thiolates as ligands to form the first azulene-containing complexes of Au(I) and azulenic self-assembled monolayer films on Au(111), see Figures 2 and 3.[12]

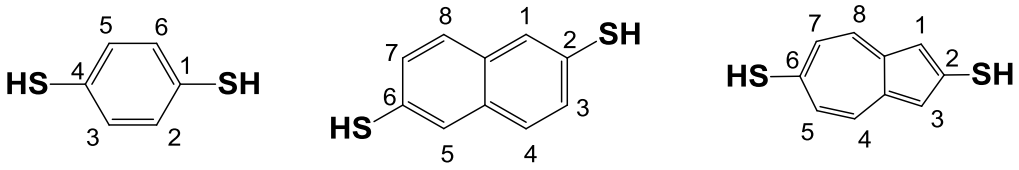


Figure 1: Atom numbering schemes for 1,4-dimercaptobenzene (left), 2,6-dimercaptonaphthalene (center), and unknown 2,6-dimercaptoazulene (right). [Reproduced by permission of The Royal Society of Chemistry] [13]

$R^1 = R^2 = H$ (**II.1a**)
$R^1 = R^2 = CO_2Et$ (**II.1b**)
$R^1 = H$, $R^2 = CO_2Et$ (**II.1c**)
$R^1 = R^2 = CN$ (**II.1d**)

$R^1 = R^2 = H$ (**II.2a**)
$R^1 = R^2 = CO_2Et$ (**II.2b**)

Figure 2: Isolable mercaptoazulenes known to date.[12,14-17] [Reproduced by permission of The Royal Society of Chemistry] [13]

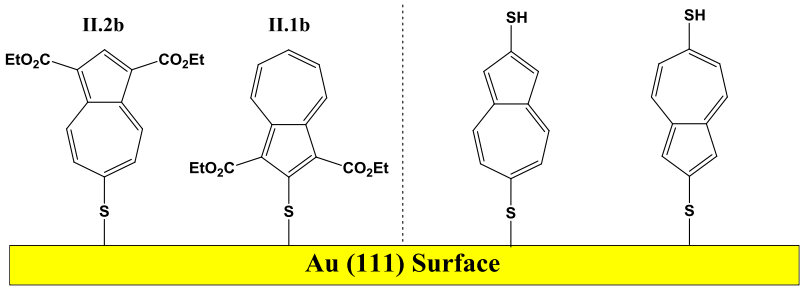


Figure 3: Self-assembled monolayer (SAM) on a Au(111) surface, where (on the left side) compounds **II.1b** and **II.2b** are absorbed onto the surface which orient perpendicular to the surface. On the right side, hypothetical 2,6-dimercato-azulene bound with either the 2- or 6-mercapto terminus.

While the di-mercaoptoazuleneic motif is an attractive target for self-assembled monolayer studies, the orientation of the azulene core needed to be controlled as it could attach to the surface in either orientation, see Figure 3.[18] As a feature of azulene is its natural dipole moment, it is necessary to ensure one orientation on the surface to adequately determine the conductivity and potential diode-like behavior. To this end, rigorous theoretical studies were undertaken to probe whether a sufficient energetic barrier could be designed into the 1- and 3-positions of the azulenic motif. As an extension of Chapter 1 of this dissertation, studies looking at the exchange in mono- and bi-metallated complexes with [Ph_3PAu^I] fragments were additionally undertaken.

Experimental

General procedures, starting materials and equipment

Unless specified otherwise, all operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air. Solutions were transferred via stainless steel needles

(cannulas) whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line. Both CH_2Cl_2 and CD_2Cl_2 were distilled over CaH_2. Deuterated chloroform was distilled over P_2O_5. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Other solvents were used as received from commercial sources.

NMR spectra were acquired on a 400 or 500 MHz Bruker DRX spectrometer equipped with a X-channel observe quadruple nuclei probe. ^{1}H and ^{13}C NMR chemical shifts are given with reference to residual solvent resonances relative to $SiMe_4$. ^{31}P NMR chemical shifts are referenced externally to 85% aqueous H_3PO_4 (a sealed capillary tube containing 85% aqueous H_3PO_4 was inserted into each sample tube subject to ^{31}P NMR analysis). UV-Vis spectra were recorded at 24 °C using a CARY 100 spectrophotometer.

2-Mercaptoazulene (**II.1a**) [12], 2-mercapto-1,3-diethoxycarbonylazulene (**II.1b**) [12], 6-bromo-1,3-diethoxycarbonylazulene [19], 6-mercapto-1,3-diethoxycarbonylazulene (**II.2b**) [13,20], 2-amino-6-bromo-1,3-diethoxycarbonylazulene (**II.3**) [21], 2,6-dichloro-1,3-diethoxycarbonylazulene (**II.4**) [13,20], 2-chloro-6-mercapto-1,3-diethoxycarbonylazulene (**II.5**) [13,20], 2,6-di(2-methoxycarbonylethylthio)-1,3-diethoxycarbonylazulene (**II.6**) [13,20], 2-hydroxy-6-bromo-1,3-diethoxy-carbonylazulene (**II.7**) [22], dimercapto-1,3-diethoxycarbonylazulene (**II.9**) [13,20], $[Ph_3PAu]$(1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate) (**II.10**) [13,20], $[Ph_3PAu]_2(\eta^1{:}\eta^1$-1,3-diethoxycarbonyl-2,6-azulenedithiolate) (**II.11**) [13,20], and $Au(PPh_3)Cl$ [23] were prepared according to literature procedures. Other reagents were obtained from commercial sources and used as received.

Density Functional Theory Calculations

All density functional theory (DFT) calculations were performed using the ORCA (v.2.9.1) program.[24] Geometric optimizations for the gold complexes were performed spin-restricted using the BP86 functional[25,26] with a triple-zeta valence with polarization (TZVP) basis set.[27,28] The resolution of identity approximation (RI) was used along with the SV/J auxiliary basis set [Ahlrich's Coulomb fitting basis for split valence basis set with polarization (SVP)],[29] and the Zero-Order Regular Approximation (ZORA).[30] Single point energy and time-dependent DFT (TD-DFT) calculations were then performed using the B3LYP functional[31-33] with ZORA, a TZVP basis set, and a TZV/J auxiliary basis set [Ahlrich's Coulomb fitting basis for TZVP].[18]

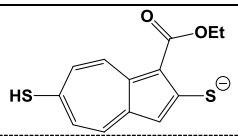
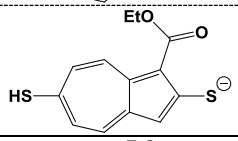
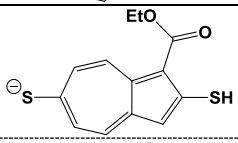
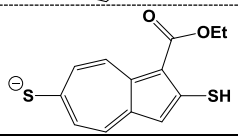
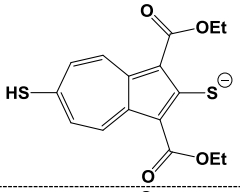
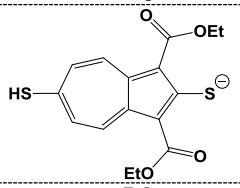
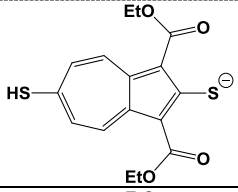
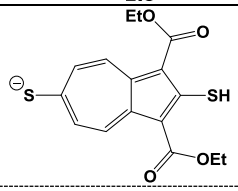
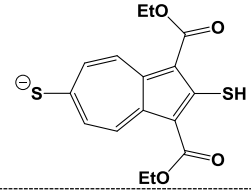
Geometric optimizations and single point energy calculations for the strictly organic molecules were performed using the B3LYP functional with a TZVP basis set, the RI 'chain of spheres' algorithm (RIJCOSX), and a TZV/J auxiliary basis set.[29,31-34] The solvation effects of tetrahydrofuran (THF) [$\varepsilon = 7.25$] were modeled using the conductor-like screening model (COSMO), as implemented in ORCA.[35] For the structures featuring ethyl ester substituents attached to the azulenic framework, multiple conformations of the ester groups were probed to ensure selection of the lowest energy scenarios. The BP86 functional was chosen for geometric optimizations as it has been shown to be quite accurate for inorganic systems, while B3LYP was chosen to calculate the total energies again for its proven accuracy.[36] Molecular images and orbital surface contour plots were produced using the Molekel (v.5.4.0.8) program with isodensity values set at ±0.03.[37] The final Cartesian coordinates for all optimized structures are provided in the appendix (Tables A2.1 – A2.16 & A2.18 – A2.31).

Results and Discussion

All transition metal complexes of dimercaptoarenes known to date involve coordination of both of their S-termini through the formation of the thiolate junctions between the metal centers and the aromatic linker. Given the currently accessible substitution patterns in 2- and 6-mercaptoazulenes (Figure 2), several hypothetical isomeric pairs of functionalized 2,6-dimercaptoazulenic conjugate bases were considered by density functional theory (DFT).

In order to adequately model the stability of the 2- vs 6- thiolate energies for the various azulene derivatives studied, the orientation of the ester groups at the 1- or 1,3- positions needed to be optimized independently. The reason being that DFT will in fact find the local minima pertaining to a given ester group configuration. In hopes of identify the global minima of the systems, some initial optimizations were undertaken. Table 1 shows the various optimizations completed for the strictly organic anions at the B3LYP / TZVP level of theory (all of which were in the gas phase). Of note is the interesting correlation that the 2-thiolate-azulenes tend to favor the ethoxy tail nearby, while the 2-mercapto-azulenes favor a hydrogen bonded interaction with the carbonyl. Following the work focused on the organic molecules, the inorganic gold(I) complexes were subjected to the same level of study but optimized at the BP86 / TZVP level of theory, see Table 2. In the case of the 1-ethoxycarbonyl-azuelenes, the ester group configuration was maintained from the free organic analogue in the case of the 2-mercapto-6-thiolate-azulene. Again, a correlation is observed linking the 2-thioalte-azulene complexes to favoring the ethoxy tail nearby.

Table 1: Ester group orientations considered and optimized using B3LYP / TZVP criteria (in the gas phase) to find the lowest energy confirmation for assembling Table 3 (see also Tables A2.3 – A2.6 & A2.18 – A2.23).

Molecules	Energy Difference (kcal / mol)
	0
	+2.8
	0
	+2.9
	0
	+1.7
	+5.3
	0
	+0.5

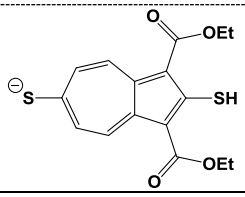
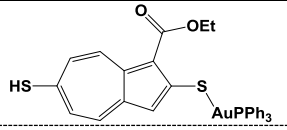
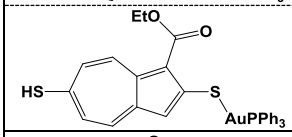
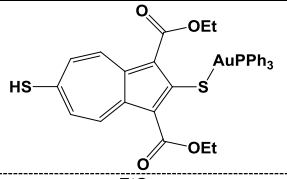
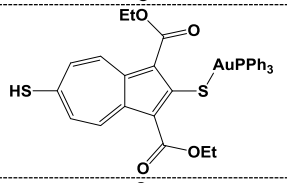
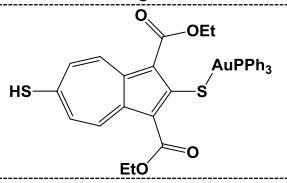
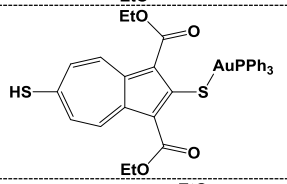
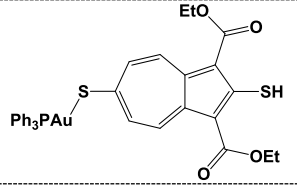
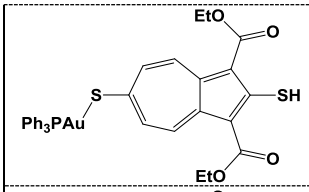
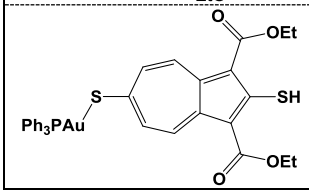
	+2.1

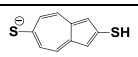
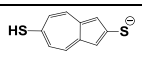
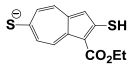
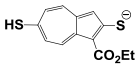
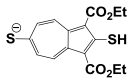
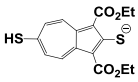
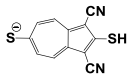
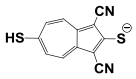
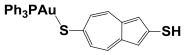
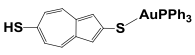
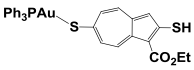
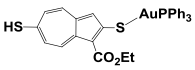
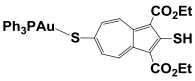
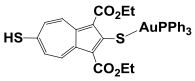
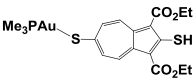
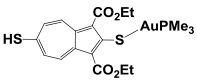
Table 2: Ester group orientations considered and optimized using B3LYP / TZVP criteria (in the gas phase) to find the lowest energy confirmation for assembling Table 3 (see also Tables A2.11 – A2.14 & A2.24 – A2.29).

Complexes	**Energy Difference (kcal / mol)**
	0
	+1.3
	0
	+1.3
	+1.6
	+2.8
	0

	+1.6
	+2.4

In Table 3, the relative energies of the anions may be related to the acidity strengths of the SH groups being deprotonated. In the case of the simplest pair, 2-mercapto-6-azulenethiolate appears to be slightly more stable than its 6-mercapto-2-azulenethiolate congener, see also Figure 5. This can be explained by the direction of the azulenic dipole (e^--rich 5-membered ring / e^--poor 7-membered ring) and the possibility of resonance stabilization of the former anion to give the aromatic cyclopentadienide-like structure shown in Figure. 4. Introduction of cyano substituents at the 1,3-positions of the azulenic nucleus results in little change in the stabilities of these isomeric mercaptoazulene thiolates. The cyano substituent (Hammet σ_p = +0.66) and the ethyl ester substituent (Hammet σ_p = +0.45) have similar electron withdrawing capabilities; however, the cyano group is unable to form an intramolecular hydrogen bond with the 2-mercapto terminus.[38] The comparison between Figures 5C and 5D shows the effect of the hydrogen bonding on the stabilization of the 2-mercapto terminus. On the other hand, the 2-thiolate isomer becomes substantially less stable than the 6-thiolate isomer upon 1,3-diethoxycarbonyl substitution due to unfavorable electrostatic interaction of the 2-thiolate anion with the carboxylate units, which are pushed out of the azulenic plane by 33±4° (*vide infra*).

Table 3: DFT-calculated energy differences ($\Delta E = E_B - E_A$) in kcal/mol between isomeric structures B and A in the gas phase and in THF.[a] [Reproduced by permission of The Royal Society of Chemistry] [13]

A	B	ΔE_{gas} [a]	ΔE_{THF} [a]
		4.8	3.2
		11.9	9.8
		16.1	14.4
		7.17	3.31
		0.3	0.5
		4.7	2.8
		9.9	8.9
		9.7	9.4

[a] ORCA (v.2.9.1) SP: B3LYP/TZVP. See Tables A2.1-A2.16 and Figures 5-9.

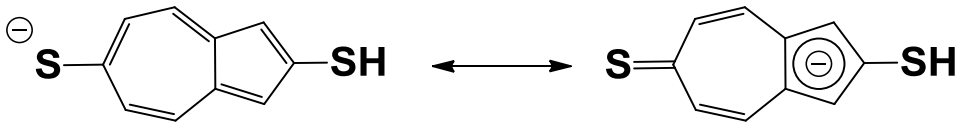


Figure 4: Resonance stabilization of 2-mercapto-6-azulenylthiolate. [Reproduced by permission of The Royal Society of Chemistry] [13]

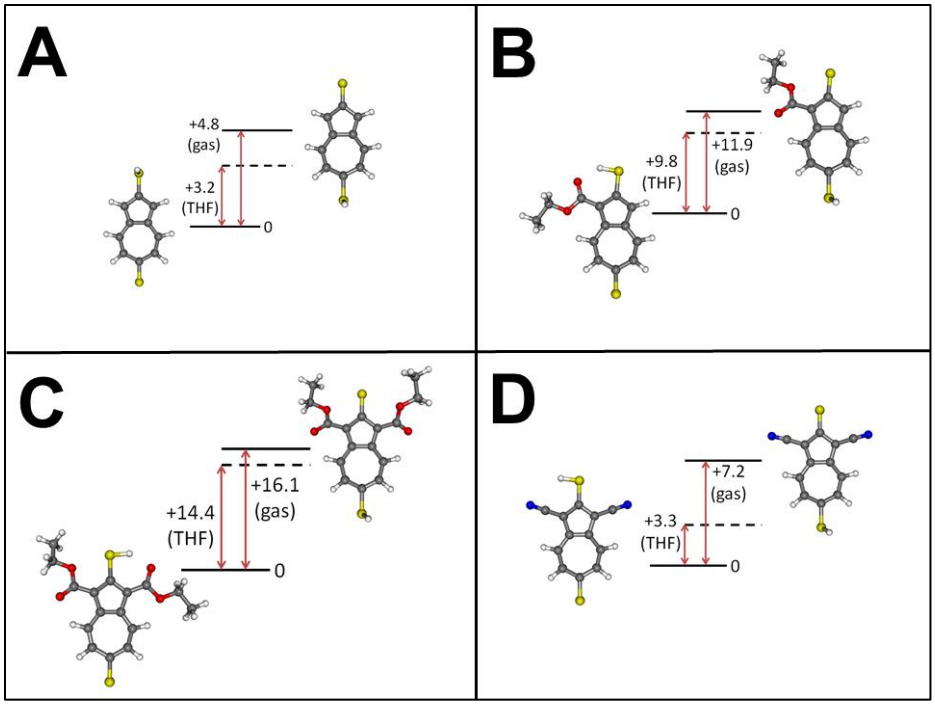


Figure 5: DFT-calculated energy differences (ΔE, in kcal/mol in the gas phase and THF) between hypothetical isomeric compounds: A) 2-mercapto-6-azulenethiolate anion vs. 6-mercapto-2-azulenethiolate anion; B) 2-mercapto-1-ethoxycarbonyl-6-azulenethiolate anion vs. 6-mercapto-1-ethoxycarbonyl-2-azulenethiolate anion; C) 2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate anion vs. 6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate anion; D) 2-mercapto-1,3-dicyano-6-azulenethiolate anion vs. 6-mercapto-1,3-dicyano-2-azulenethiolate anion (See also Tables A2.1 – A2.8).

Interestingly, complexation of the "parent" 2-mercapto-6-azulenethiolate and 6-mercapto-2-azulenethiolate ligands with the Ph_3PAu^I fragment is predicted to yield isoenergetic adducts (Figure 6), whereas the energy difference between the corresponding complexes featuring one ester substituent is marginal at best (Figure 7). However, the isomeric gold(I) triphenylphosphine complexes of the mercaptoazulene thiolates possessing two ester substituents are suggested to have markedly different relative energies. The less favorable isomer involves binding of the Au^I unit to the 2-thiolate junction and features substantial steric congestion, which moves the carboxylate groups out of the aromatic plane, thereby disrupting their conjugation

with the azulenic ring (Figure 8). Replacing the PPh_3 ligand with a smaller phosphine (PMe_3) has no effect on the predicted relative stabilities of these complexes (Figure 9). In the case of the replacement of the triphenylphosphine (PPh_3) with trimethylphosphine (PMe_3), the same ester group orientation was maintained from the already lowest energy configuration determined for the PPh_3 complexes. Thus, it might be possible to access mononuclear adducts of a dimercaptoarene by employing the 2,6-dimercapto-1,3-diesterazulene design.

Though there is significant distortion and steric strain between the 2-thiolate complexes and the ester groups, gold(I) complexes can be still formed. To illustrate this, another DFT study comparing the energy difference between 2- vs. 6-thiolate-azulene (dcpm)bis-gold(I) complexes, see Figure 10 (dcpm = bis(dicyclohexylphosphino)methane). Clearly, the 2-thiolate complex is unfavored by over 20 kcal/mol; yet Dr. Alexander Vorushilov was able to synthesize and crystalize both complexes.[39] Additionally, Chapter 1 of this work also details the formation of another 2-thiolate gold(I) complex. These complexes prove that while the regioselectivity can be controlled during deprotonation with the appropriate selection of base, both mercapto groups can in fact form gold (I) complexes.

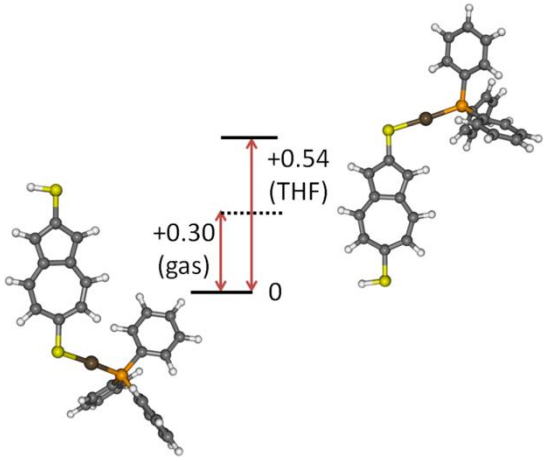


Figure 6: DFT-calculated energy differences (ΔE, in kcal/mol) between hypothetical isomeric complexes [Ph_3PAu](2-mercapto-6-azulenethiolate) and [Ph_3PAu](6-mercapto-2-azulenethiolate) in the gas phase and in THF (See also Tables A2.9 & A2.10). [Reproduced by permission of The Royal Society of Chemistry] [13]

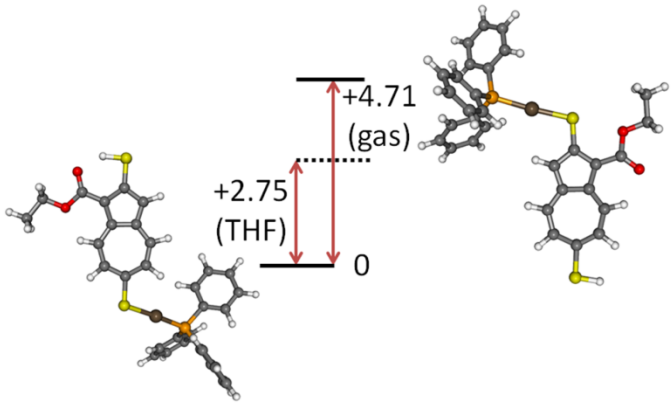


Figure 7: DFT-calculated energy differences (ΔE, in kcal/mol) between hypothetical isomeric complexes [Ph_3PAu](2-mercapto-1-ethoxycarbonyl-6-azulenethiolate) and [Ph_3PAu](6-mercapto-1-ethoxycarbonyl-2-azulenethiolate) in the gas phase and in THF (See also Tables A2.11 & A2.12). [Reproduced by permission of The Royal Society of Chemistry] [13]

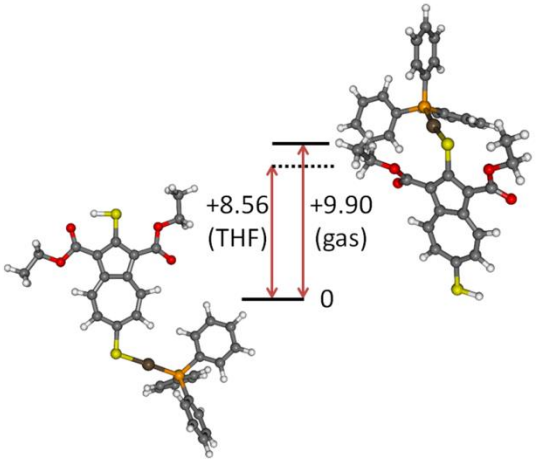


Figure 8: DFT-optimized structures of [Ph3PAu](2-mercapto-1,3-di-ethoxycarbonyl-6-azulenethiolate) and [Ph3PAu](6-mercapto-1,3-di-ethoxycarbonyl-2-azulenethiolate) **(II.10)**. The ΔE values in the gas phase and in THF are given in kcal/mol (See also Tables A2.13 & A2.14). [Reproduced by permission of The Royal Society of Chemistry] [13]

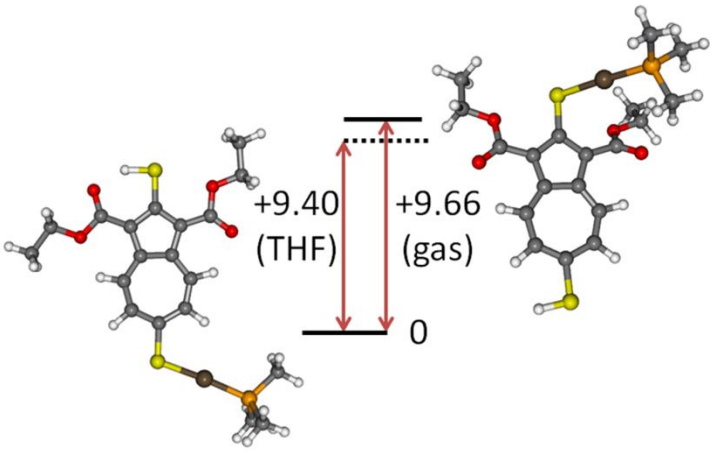


Figure 9: DFT-calculated energy differences (ΔE, in kcal/mol) between hypothetical isomeric complexes [Me_3PAu](2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate) and [Me_3PAu](6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate) in the gas phase and in THF (See also Tables A2.15 & A2.16). [Reproduced by permission of The Royal Society of Chemistry] [13]

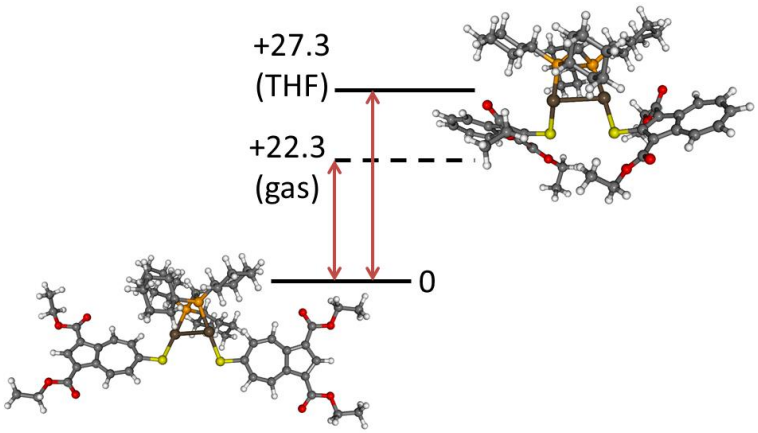


Figure 10: DFT-calculated energy differences (ΔE, in kcal/mol) between isomeric complexes [Au_2(dcpm)(1,3-diethoxycarbonyl-6-mercaptoazulene)$_2$] and [Au_2(dcpm)(1,3-diethoxycarbonyl-6-mercaptoazulene)$_2$] in the gas phase and in THF (See also Tables A2.30 & A2.31). [dcpm = bis(dicyclohexylphosphino)methane]

In the Barybin Group's 2011 communication, the X-ray structure of **II.1b** was reported.[12] In order to better appreciate the structural differences between the isomers **II.1b** and **II.2b** that affect properties of their SH groups, the solid state structure of **II.2b** was determined. Figure 11 nicely captures the most prominent difference in this regard, which is related to the orientation of the ethoxycarbonyl substituents. In both **II.1b** and **II.2b**, the carboxylate units are coplanar with the azulenic framework. In **II.1b**, the ester carbonyl groups "embrace" the 2-SH terminus. This conformation supports formation of an internal hydrogen bond by closing the six-membered ring[40] with little, if any, torsional strain (*cf.* H-bonding in *o*-mercaptobenzoates[41]). In contrast, the carbonyl bond vectors in **II.2b** are pointed toward the 4,8-H atoms of the seven-membered ring. Treatment of **II.2b** with Et_3N resulted in deprotonation of its 6-SH group (Figure 12, left), whereas **II.1b** was unaffected by excess of this amine (Figure 12, right). After considering several different bases, DBU (diazabicyclo[5.4.0]undec-7-ene), or a more powerful base, was necessary to effect the deprotonation of **II.1b** (Figure 13). Notably, the pK_a values of the conjugate acid of DBU is 4.4 - 5.5 units higher than that of Et_3NH^+ in organic solvents.[42] Thus,

the ester substituents in **II.1b** considerably mask the H^+-donor ability of the 2-SH group, deprotonation of which leads to an unfavorable interaction of the thiolate anion with the carboxylate moieties. As experimental determination of the absolute pK_a values of the various mercapto-azulenes proved tedious, a theoretical method that employed DFT was used to predict qualitative pK_a values in DMSO, see Figure 14. A more thorough procedure and discussion is undertaken in Chapter 1 of this dissertation describing the theoretical determination of pK_a values, but, suffice it to say, the relative numbers obtained are in agreement with the UV-Vis studies described above and in Figures 12 & 13. Given these results, Dr. Kolbe Scheetz, et al.[13,20] set out to synthesize the first dimercaptoazulene derivative, namely 2,6-dimercapto-1,3-diethoxycarbonylazulene, which may be viewed as a hybrid of **II.1b** and **II.2b**.

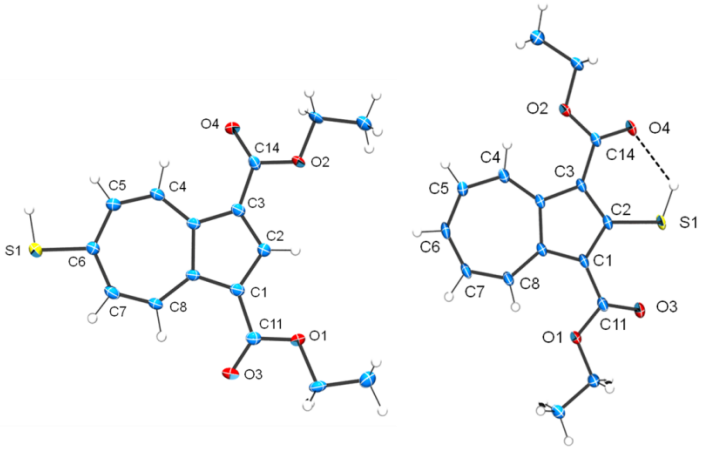


Figure 11: Left: molecular structure of one of two crystallographically independent molecules of **II.2b**.[13] Selected bond distances (Å) for **II.2b**: S(1)-C(6) 1.765(3), C(11)-O(3) 1.217(3), C(14)-O(4) 1.217(3). Right: molecular structure of **II.1b**.[16] Selected interatomic distances (Å) and angles (°) for **II.1b**: S(1)-C(2) 1.739(2), C(11)-O(3) 1.215(2), C(14)-O(4) 1.216(2), S1···O4 3.034(1), S1-H···O4 121.0. [Reproduced by permission of The Royal Society of Chemistry] [13]

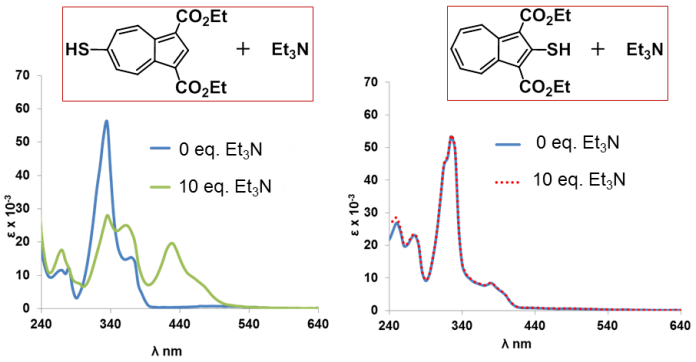


Figure 12: (Left) UV-vis spectra of **II.2b** before and after treatment with excess Et_3N in CH_2Cl_2. (Right) UV-vis spectra of **II.1b** before and after treatment with excess Et_3N in CH_2Cl_2. [Reproduced by permission of The Royal Society of Chemistry] [13]

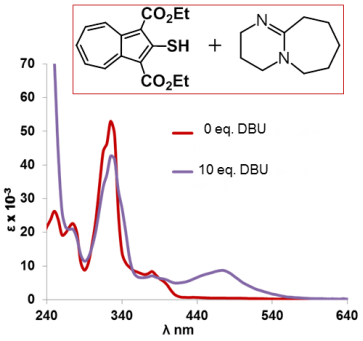


Figure 13: UV-vis spectrum of **II.1b** before and after treatment with excess DBU (DBU = diazabicyclo[5.4.0]undec-7-ene) in CH_2Cl_2. [Reproduced by permission of The Royal Society of Chemistry] [13]

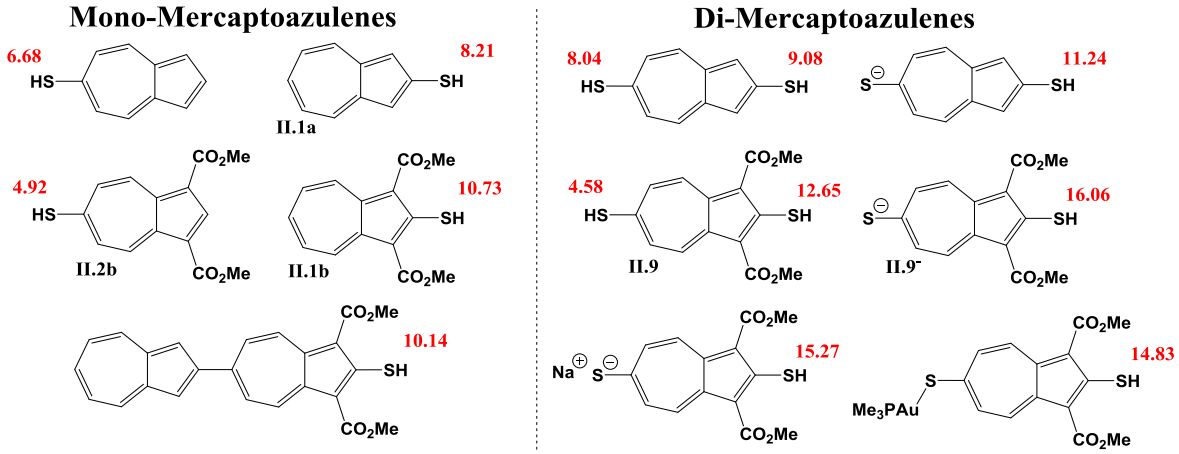
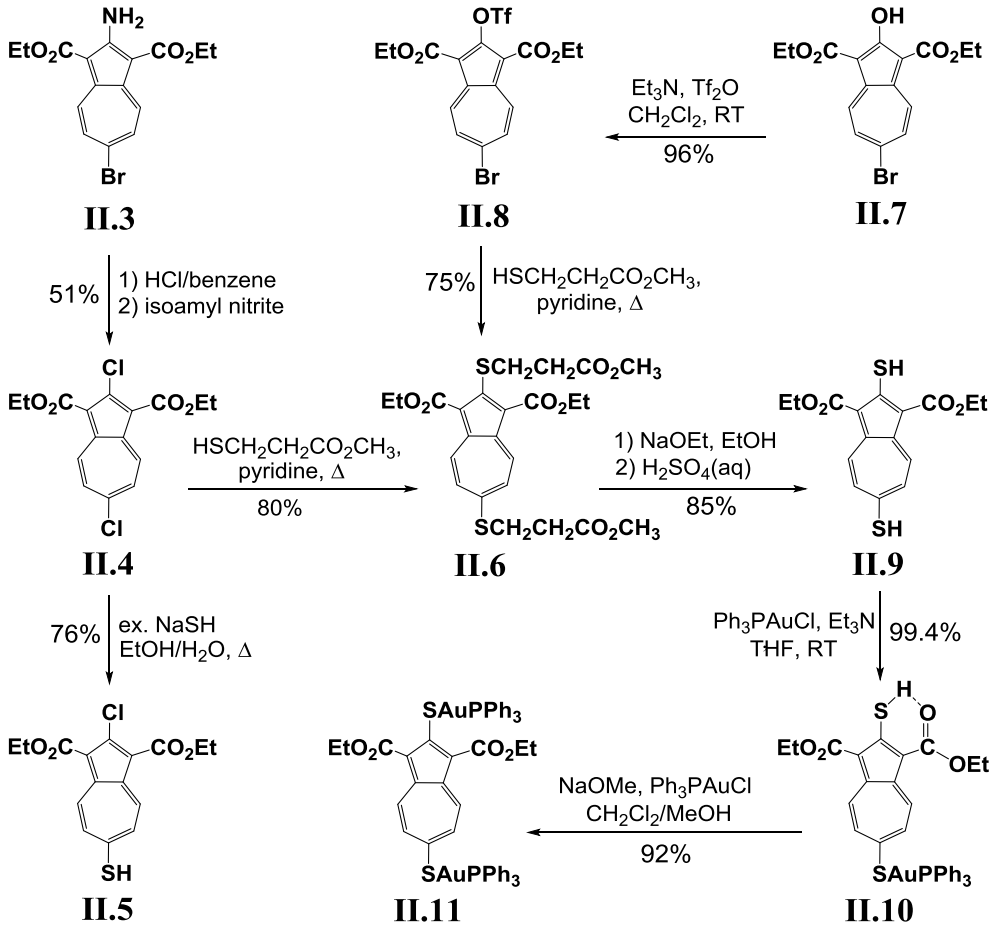


Figure 14: Theoretical determinations of pK_a in DMSO for various mono- & di-mercaptoazulenes. See Chapter 1 for further discussion.



Scheme 1: Synthesis and metallation of the 2,6-dimercaptoazulene motif. [Reproduced by permission of The Royal Society of Chemistry] [13]

After some initial roadblocks (**II.5**), the synthesis of **II.9** was completed through two common azulenic precursors, **II.3** & **II.7** in reasonable yields. Addition of 1 equiv of Et_3N to a 1:1 mixture of **II.9** and Ph_3PAuCl quantitatively produced orange mononuclear complex **II.10**. Employing excess amounts of both Et_3N and Ph_3PAuCl in this reaction still led to **II.10** as the only isolable product. The ^1H NMR and IR spectra of **II.10** are fully consistent with exclusive metallation of the 6-merapto terminus of its precursor **II.9**. The single crystal X-ray analysis of

II.10 revealed two independent molecules in the asymmetric unit that have nearly identical metric parameters (Figure 15). Complex **II.10** features the Au-S-C6 angle of *ca.* 105° and a linear geometry about the gold(I) center. The Au-P bond is about 0.05 Å shorter than the Au-S distance. All of the above metric characteristics are well within ranges of the corresponding parameters reported for a number of other complexes of the type Ph_3PAuSR.[43-45] While both carboxylate units in **II.10** are essentially coplanar with the azulenic moiety, their orientation is quite different from one another. Similar to what we observed for **II.1b**, the carbonyl oxygen atom of one of the ester groups is engaged in H-bonding interaction with the 2-SH substituent. The other ester group in **II.10** assumes a more common orientation with its carbonyl vector pointed toward the seven-membered ring. Overall, the solid state molecular arrangement of **II.10** is reasonably close to its DFT-calculated structure (Figure 8, Table A2.13). Compound **II.10** represents the first transition metal adduct of a dimercaptan ligand that features one uncomplexed SH functionality.

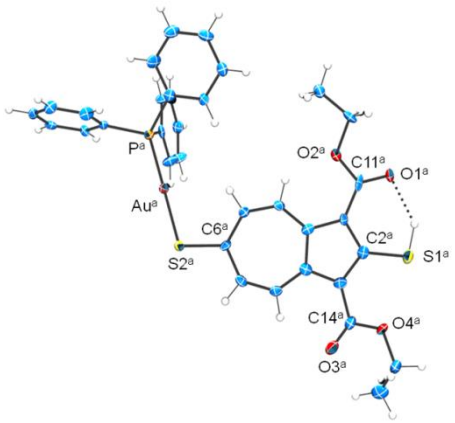


Figure 15: Molecular structure of **II.10**. One of two crystallographically independent molecules is shown. Selected interatomic distances (Å) and angles (°): Au^a-P^a 2.266(2), Au^a-$S2^a$ 2.319, $S2^a$-$C6^a$ 1.772(7), $S1^a$-$C2^a$ 1.755(7), $S1^a\cdots O1^a$ 3.030(7), P^a-Au^a-S^a 178.56(6), Au^a-$S2^a$-$C6^a$ 104.5, $S1^a$-H$\cdots O1^a$ 139.4.[20] [Reproduced by permission of The Royal Society of Chemistry] [13]

The UV-Vis spectrum of **II.10** in CH_2Cl_2 solution exhibits two intense bands at λ_{max} = 445 nm ($\varepsilon = 39.1\times10^3$ M^{-1} cm^{-1}), with a shoulder *ca.* 425 nm, and λ_{max} = 365 nm ($\varepsilon = 39.1\times10^3$ M^{-1} cm^{-1}), see Figure 16. Our Time-Dependent DFT calculations (Table A2.17) indicate that the lower energy band corresponds to the HOMO → LUMO (HOMO = Highest Occupied Molecular Orbital, LUMO = Lowest Unoccupied Molecular Orbital) transition that involves intra-ligand charge transfer within the π-system of the 2-mercapto-6-azulenylthiolate scaffold. Notably, the HOMO includes the entire 2,6-S_2-azulenic framework whereas the LUMO primarily constitutes the π*-system of the azulenic moiety with smaller contributions from the two S termini (Figure 17). Treatment of **II.10** with a large excess of Et_3N does not affect its electronic spectrum, which parallels the lack of reactivity of **II.1b** toward deprotonation with this base. On the contrary, addition of DBU to a solution of **II.10** results in depletion of the band at 445 nm accompanied by growth of a new intense feature with λ_{max} = 480 nm (Figure 18). This is consistent with deprotonation of the SH end of **II.10**, which should raise the energy of the HOMO, thereby shrinking the HOMO-LUMO gap.

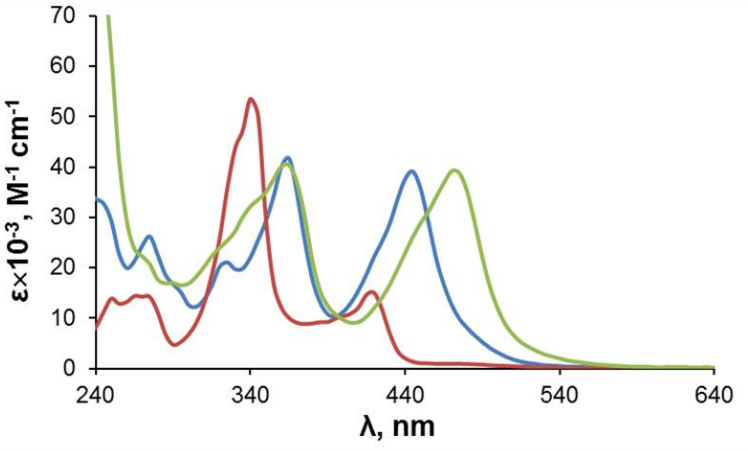


Figure 16: UV-Vis spectra of **II.9** (red), **II.10** (blue), and **II.11** (green) in CH_2Cl_2 at 25 °C. [Reproduced by permission of The Royal Society of Chemistry] [13]

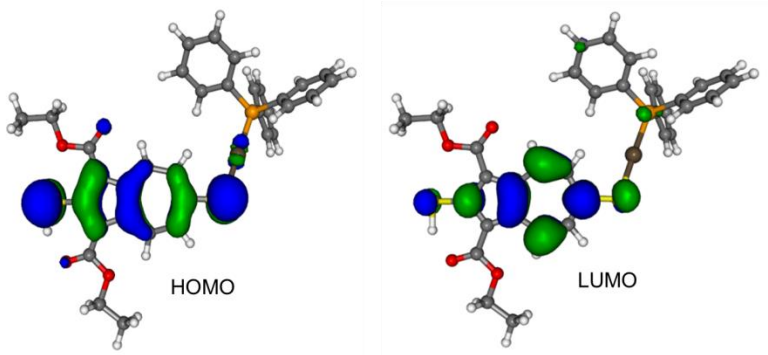


Figure 17: Frontier molecular orbitals of **II.10**. [Reproduced by permission of The Royal Society of Chemistry] [13]

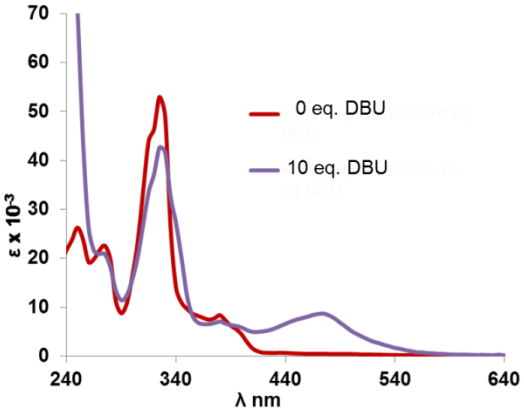


Figure 18: UV-vis spectra of **II.10** before and after treatment with excess DBU in CH_2Cl_2. [Reproduced by permission of The Royal Society of Chemistry] [13]

Addition of a 5-fold excess of NaOMe (a much stronger base than DBU) to a 1:1 mixture of **II.10** and Ph_3PAuCl afforded pure red dinuclear complex **II.11**.[13,20] Figure 16 compares the electronic spectra of **II.9**, **II.10** and **II.11**. The lowest energy band (λ_{max} = 445 nm) in the spectrum of **II.10** undergoes a 1,419 cm^{-1} red shift upon binucleation of **II.10** to form **II.11**. Notably, addition of 1 equiv. of **II.9** to a solution of **II.11** in CH_2Cl_2 cleanly generates **II.10**, as can be conveniently monitored by UV-Vis spectroscopy, see Figure 19.

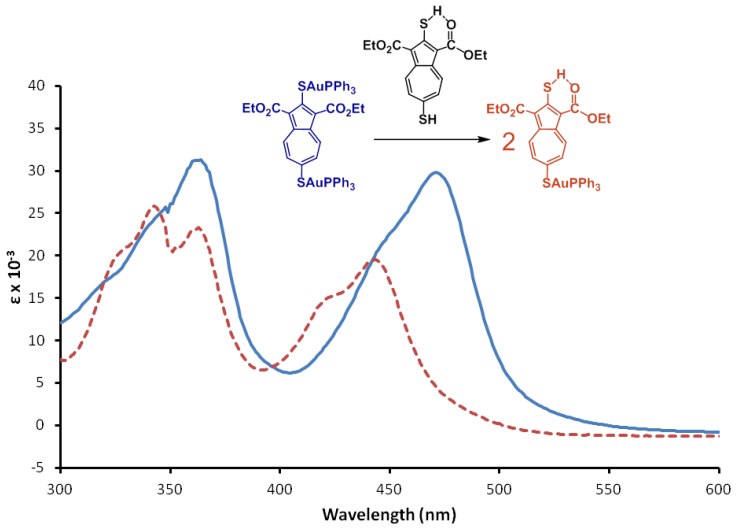


Figure 19: UV-Vis spectrum of **II.11** (blue, solid) and the spectrum after the addition of 1 eq. of **II.9** producing 2 eq. of **II.10** (red, dashed) in CH_2Cl_2 at 25 °C.

While the $^{31}P\{^{1}H\}$ NMR spectrum of **II.10** in CD_2Cl_2 exhibits a singlet at 37.89 ppm vs. 85% aq. H_3PO_4, the ^{31}P NMR signature of **II.11** at 22 °C consists of a single, albeit broad, resonance at 37.19 ppm. This broad peak gradually splits into two upon cooling the sample to give singlet resonances at $\delta(^{31}P)$ = 37.95 and 36.19 ppm at -40 °C (Figure 20). The coalescence temperature for this exchange process is about 0°C. The chemical shift of the more downfield peak in the low temperature ^{31}P NMR spectrum of **II.11** is practically identical to that documented for the ^{31}P signal of **II.10**. Therefore, this resonance corresponds to the $AuPPh_3$ unit bound to the 6-S end of **II.11**. In principle, the exchange of the ^{31}P environments in solution of **II.11** can be rationalized through either reversible scission of the inequivalent Au-PPh_3 bonds in **II.11**, or heterolytic cleavage of the Au-S bonds to induce scrambling of the $[AuPPh_3]^+$ fragments. Previous studies on the ligand exchange involving phosphine-thiolate complexes of Au(I)[46] suggest that the latter possibility is more likely. A study where 1 eq. of PPh_3 was added to **II.10** erased the 37.89 signal from the isolated complex in the ^{31}P NMR, see Figure 21B. This

loss of signal indicates that there could be an exchange reaction occurring and suggests 22°C is the coalescence temperature, if so. Interestingly, addition of 2 equiv. of PPh_3 ($\delta(^{31}P)$ = -5.53 ppm) to a sample of **II.11** ($\delta(^{31}P)$ = -37.19 ppm) at 25 °C produced a ^{31}P NMR spectrum (Figure 22) that features just one broad resonance at 17.94 ppm. Given that the mid-point between the ^{31}P NMR chemical shifts of **II.11** and PPh_3 is *ca*. 15.8 ppm, it appears that another Au(I)-phosphine species must be present in the equilibrium mixture prepared from **II.11** and 2 equiv. of PPh_3 that reduces the overall presence of free PPh_3 in the mixture. Displacement of the thiolate junctions in **II.11** by PPh_3 to form the well-known $[Au(PPh_3)_2]^+$ cation ($\delta(^{31}P)$ = 33.49 ppm[47]) may be reasonable to suggest.[46]

In light of the studies on complex **II.11** with electronic spectroscopy (Figure 19) and the numerous ^{31}P NMR spectra, a likely reaction mechanism can be proposed, shown in Figure 23. The main complex of II.11 does form a slight equilibrium with a bond scission between the 2-thiolate-azulene anion and the $Au(PPh_3)^+$ fragment. Another equivalent of free **II.9** ligand can be added and deprotonated at the 6-mercapto terminus by the 2-thiolate-azulene anion forming one equivalent of **II.10** and a 6-thiolate-azulene anion. The $Au(PPh_3)^+$ fragment can subsequently combine with the 6-thiolate-azulene anion to produce the second equivalent of **II.10**.

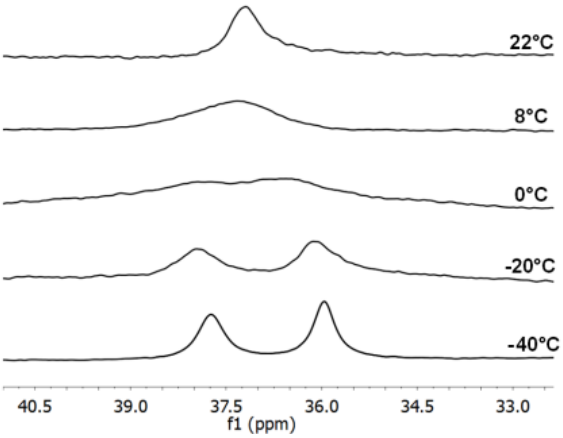


Figure 20: Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of **II.11** in CD_2Cl_2. [Reproduced by permission of The Royal Society of Chemistry] [13]

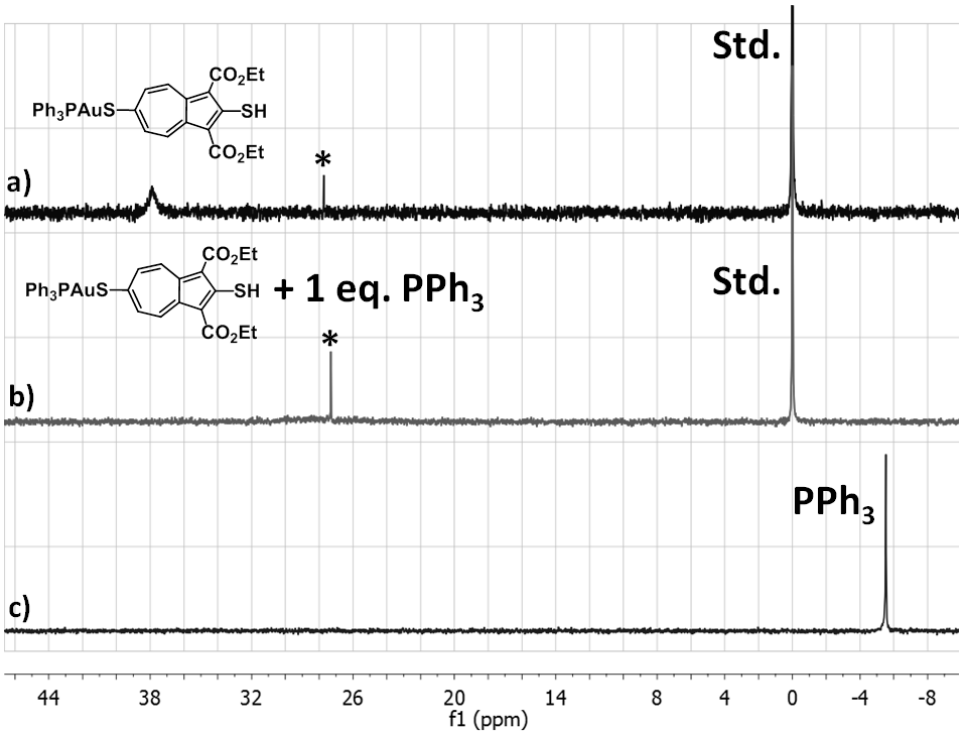


Figure 21: $^{31}P\{^{1}H\}$ NMR spectra (202 MHz, CD_2Cl_2, 22 °C, 85% aq. H_3PO_4 externally referenced, denoted Std.) of (a) **II.10**, (b) **II.10** + 1 eq. PPh_3, and (c) PPh_3. Asterisks denote an $O{=}PPh_3$ impurity.

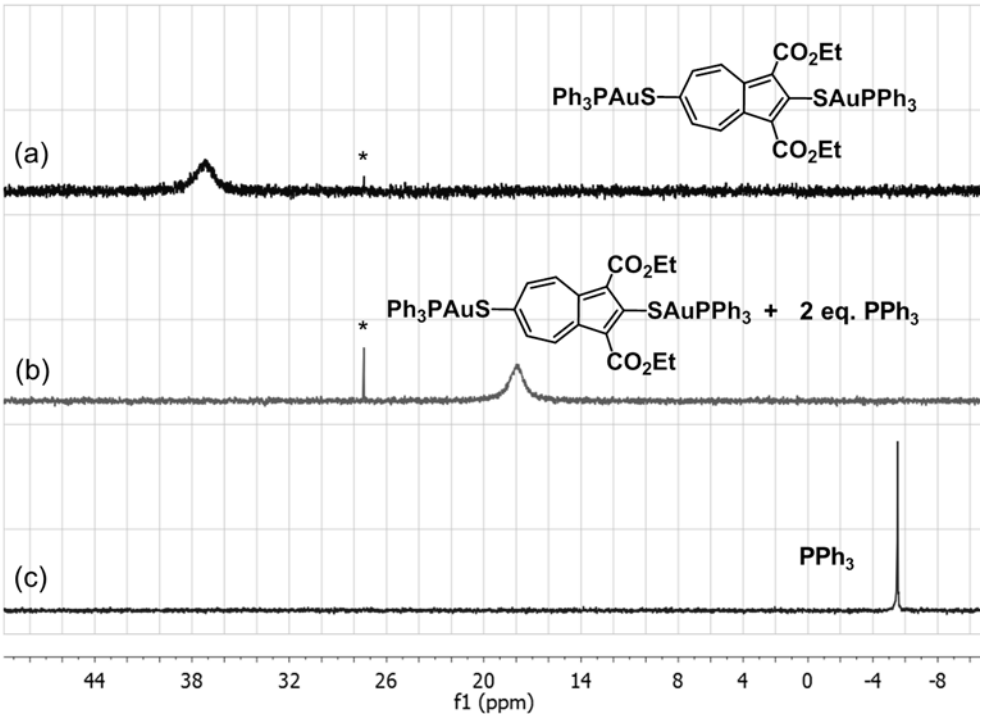


Figure 22: $^{31}P\{^{1}H\}$ NMR spectra (202 MHz, CD_2Cl_2, 22 °C, 85% aq. H_3PO_4 external reference) of (a) **II.11**, (b) **II.11** + 2 eq. PPh_3, and (c) PPh_3. Asterisks denote an $O=PPh_3$ impurity. [Reproduced by permission of The Royal Society of Chemistry] [13]

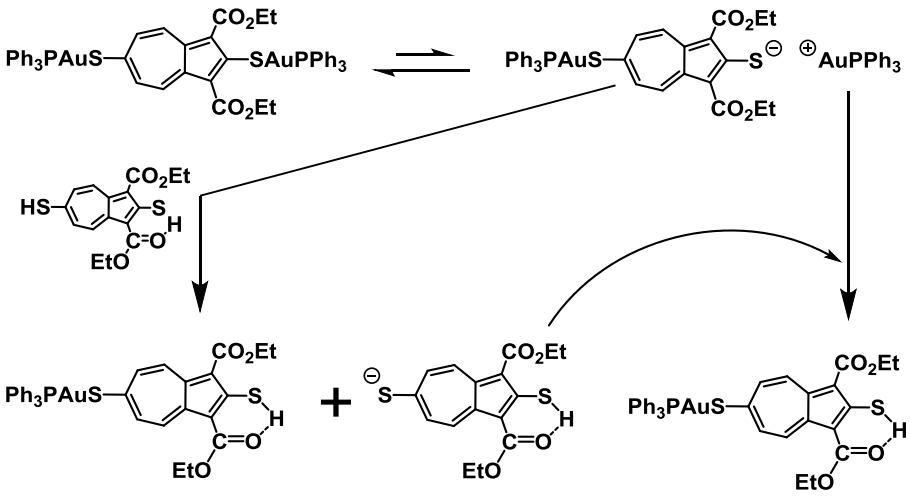


Figure 23: Proposed reaction mechanism showing how **II.11** and **II.9** can combine to form 2 eq. of **II.10**.

Conclusion

The theoretical assessment of the reactivities of 2,6-dimercapto-1,3-diethoxycarbonylazulene **II.9**, a rare example of an unsymmetric linear dimercaptoarene, and related species toward deprotonation and subsequent metallation with Au(I) proved invaluable in guiding the synthetic efforts to access organometallic ensembles featuring an azulenic molecular linker with thiolate junctions. The two SH termini in **II.9** exhibit profoundly different acidities, which permits completely regioselective metallation of its 6-SH terminus. The origin of this remarkably regioselective complexation of the 2,6-dimercaptoazulene scaffold bearing 1,3-diethoxycarbonyl substituents was uncovered through a systematic density functional theory analysis of a series of mono-deptotonated 2,6-dimercaptoazulene derivatives. The ester substituents at the 1,3-positions of the 2,6-dimercaptoazulenic framework are critical for ensuring a substantial advantage (*ca.* 15 kcal/mol) in the stability of the corresponding conjugate base formed via deprotonation of its 6-SH terminus rather than the 2-SH end. This energetic preference of 2-mercapto-1,3-diethoxycarbonyl-6-azulenyl thiolate as compared to its 2-thiolate isomer is preserved upon complexation of the thiolate junction with $[R_3PAu^I]$.

The mononuclear Au(I) complex **II.10** forms exclusively upon deprotonation of **II.9** with a mild base, such as triethylamine, followed by treatment with $ClAuPPh_3$. Its 2-SH and 6-$SAuPPh_3$ termini do not undergo scrambling to generate the more sterically congested isomer that would feature 6-SH and 2-$SAuPPh_3$ ends. The latter structure would be about 10 kcal/mol less stable and involve the substantially more acidic mercapto functionality. Binucleation of the mononuclear complex **II.10** affords the dinuclear Au(I) complex **II.11**, which serves as a unique unsymmetric platform to observe the exchange of gold-bound thiolates by employing a single compound. Unlike the exchange of thiolate ligands adsorbed on Au surfaces[48-50], this molecular

platform is amenable to convenient studies in solution. The variable temperature ^{31}P NMR spectra of **II.11** indicate fast exchange of the ^{31}P nuclei in this complex at ambient temperature. While it is tempting to invoke dissociations of the Au-P bonds to account for the above exchange, careful ^{31}P NMR analysis of a 1:2 mixture of **II.11** and free PPh_3 strongly suggests that a reversible heterolytic scission of the Ph_3PAu-S bonds is responsible for scrambling of the ^{31}P environments in **II.11**.

The approach presented in this Chapter nicely illustrates how synergistic consideration of computational, spectroscopic, and synthetic aspects ultimately leads to successful access of the molecular rectifier platform sought by theorists for a number of years. Future efforts will be focused on determining whether discrimination between the SH termini of **II.9** also occurs upon adsorption of this nonbenzenoid unsymmetric dimercaptoarene on gold and other metal surfaces. Extrapolating the acid/base chemistry of **II.9** described in this Chapter to develop its chemistry on metallic surfaces should be taken *cum grano salis*, especially, because the mechanism of the S-H bond activation in the latter case may not necessarily involve the heterolytic dissociation of the S-H unit. Establishing self-assembly of **II.9** and/or related motifs on metallic gold with controlled orientation of the azulenic dipole will provide an excellent opportunity to probe conductivity characteristics of the 2,6-azulenic platform. Notably, **II.9** is now the third example of the linear azulenic linker featuring junction groups at its 2,6-positions. The π^* systems of the other two, namely 2,6-diisocyanoazulene and 2,6-azulenedicarboxylate, have been recently shown by the Barybin group to be effective in mediating charge delocalization between low-valent, electron-rich metal units.[12,51]

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CHAPTER 3

The Linear 6,6'-Biazulenic Platform Featuring Isocyanide Termini along its Molecular Axis is Accessible in Three Different Redox States

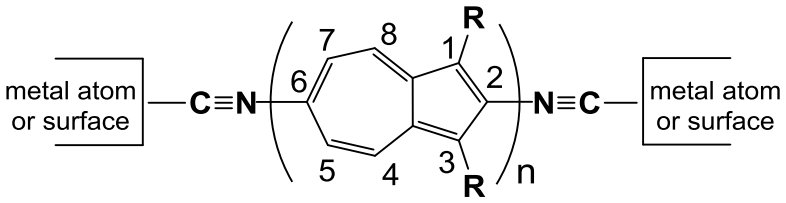
Portions of this work were published in the
Journal of the American Chemical Society, **2010**, *132*, p. 15924-15926.

Abstract

The key step in accessing the title species (**III.1c**), the first non-benzenoid diisocyanobiaryl, involved an unexpected homo-coupling of a 6-bromoazulene derivative. The unusual $2e^-$ redox behavior of **III.1c** was addressed electrochemically and computationally. The shifts in energies of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions for a series of related 6,6'-biazulenyl derivatives correlate with the e^--donating/withdrawing strength of their 2,2'-substituents but follow opposite trends. Bimetallic complexation of **III.1c** through the -NC termini can be readily achieved. In addition, **III.1c** adsorbs end-on (η^1) on the Au(111) surface via one of its -NC groups to form a 2 nm-thick film. The reduced anionic and dianionic states of both **III.1c** and its acetylene bridged analogue (**III.2c**) were explored using theoretical, EPR, and UV-Vis-NIR methods.

Introduction

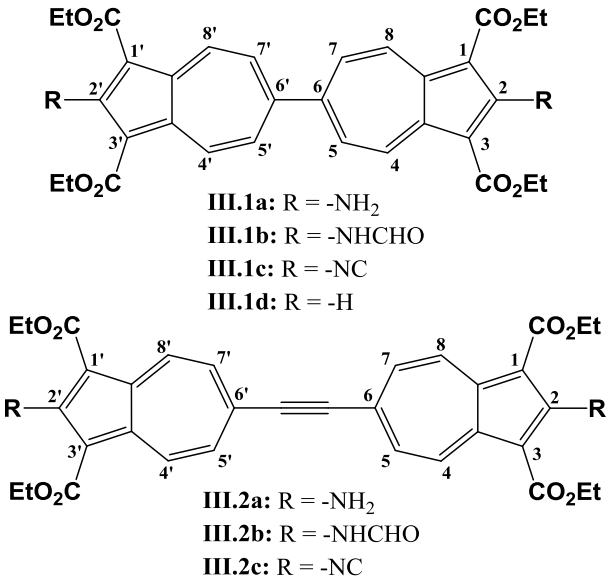
Azulene is an unusual aromatic hydrocarbon ($C_{10}H_8$) that comprises an edge sharing combination of 5- and 7-membered sp^2-carbon rings. The azulenic and polyazulenic motifs constitute attractive building blocks in the design of redox addressable, optoelectronic, and conductive materials.[1-8] Unlike the frontier molecular orbitals of benzenoid aromatics, the HOMO and LUMO of azulene are not mirror related and feature mutually complementary density distributions (HOMO = Highest Occupied Molecular Orbital, LUMO = Lowest Unoccupied Molecular Orbital).[7] This leads to a remarkably low $S_0 \rightarrow S_1$ excitation energy for azulene derivatives and enables topological asymmetry in the electron and hole transport regimes for azulene-based frameworks.[1-8]



Scheme 1: Linear diisocyanoarene linkers targeted by the Barybin group. [Reprinted with permission. Copyright 2010 American Chemical Society.][9]

Coordination and surface chemistry of linear benzenoid diisocyanoarenes containing one or more linked aromatic rings has been the subject of growing experimental and theoretical interest,[10-12] particularly in the context of developing advanced materials that may support charge delocalization and transport at the nanoscale.[13-17] The Barybin group has recently engaged in the quest for a novel class of linear diiscyanoarene linkers based on the nonbenzenoid 2,6-azulenic framework as represented by the homologous series Scheme 1.[6,18,19] For n = 1 (R = -CO_2Et) in Scheme 1, the orientation of the azulenic dipole can be controlled through regioselective installation and coordination of the isocyanide junction groups.[19] For n = 2, three different linear diisocyanobiazulenyl scaffolds can be envisioned: two symmetric featuring the 6,6' or 2,2' connectivity of the azulenic moieties and one asymmetric having the 2,6' central C-C bond. Currently, very few 2,2'-, 6,6'-, and 2,6'-biazulenyl derivatives are synthetically accessible.[20-24] Herein, the chemistry of the first member of the linear diisocyanobiazulenyl family that is *formally* derived by linking two 1,3-diethoxycarbonyl-2-isocyanoazulene[18] molecules is introduced. To the best of the author's knowledge, the title species is the first structurally characterized functionalized linear biazulenyl[20-24] compound, but also the sole example of a crystallographically addressed biazulenyl motif of any connectivity not embedded into a larger rigid framework.[25] Notably, the X-ray crystal structure of terazulene, which contains three linearly connected unsubstituted azulenic units and behaves as an efficient n-type field-effect

transistor, has been very recently published in *J. Am. Chem. Soc.* by Nakayama *et al*.[26] Scheme 2 identifies the compounds described in this Chapter, including the strain-free analogues of **III.1a-d** (**III.2a-c**).



Scheme 2: Numbering legend for the compounds discussed in this chapter and the carbon atom numbering scheme for the azulenic scaffolds.

Experimental

General procedures and starting materials

Unless specified otherwise, all operations were performed under an argon atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air. Solutions were transferred via stainless steel cannulas whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line. CH_2Cl_2, CH_3CN, and $NH(^iPr)_2$ were distilled over CaH_2. THF and

Toluene were distilled over Na/benzophenone. Following purification, all distilled solvents were stored under argon.

Solution infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with samples sealed in 0.1mm gas tight NaCl cells. NMR spectra were acquired on a 400 or 500 MHz Bruker DRX spectrometer equipped with a X-channel observe quadruple nuclei probe. ^{1}H and ^{13}C chemical shifts are given with reference to residual ^{1}H and ^{13}C solvent resonances relative to Me_4Si. ^{14}N chemical shifts were referenced to an external DMF standard relative to NH_3 (liq.). UV-Vis spectra were recorded in CH_2Cl_2 at 24°C using a CARY 100 spectrophotometer, and spectra of **III.1a-d** and **III.2a-c** can be found in Figures A3.36 - A3.42. UV-Vis-NIR spectra were recorded in THF or CH_3CN at 24°C using an air-free quartz cuvette in a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were obtained using a Cary Eclipse Fluorescence Spectrophotometer at *ca.* 10^{-5} molar concentrations and with excitation and emission slit widths set to 5 nm. The excitation and emission spectra were corrected for instrumental variation whenever possible (220 to 600 nm or 45,454 to 16,667 cm^{-1}). Low temperature operation was achieved by using an Oxford OptistatDN cryostat under a nitrogen atmosphere. Mass spectra were analyzed on a VG Analytical ZAB or a LCT Premier ESI-MS by the KU Mass Spectrometry Laboratory. Elemental analyses were carried out by Chemisar/Guelph Chemical Laboratories Ltd, Ontario, Canada and Columbia Analytical Services, Tucson, Arizona. Self-assembled monolayer studies were carried out by Dr. Brad M. Neal and Dr. Tiffany R. Maher.[9,27]

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments on 2 x 10^{-3} M solutions of selected compounds in CH_2Cl_2 were conducted at room temperature using an EPSILON (Bioanalytical Systems, INC., West Lafayette, IN) electrochemical workstation. The

electrochemical cell was placed in an argon-filled Vacuum Atmospheres dry-box. Tetrabutylammonium hexafluorophosphate (0.1 M solution in CH_2Cl_2) was used as the supporting electrolyte. CV data was recorded using a three component system consisting of a platinum working electrode, platinum wire auxillary electrode, and a glass encased non-aqueous silver/silver chloride reference electrode. The reference Ag/Ag^+ electrode was monitored with the ferrocenium/ferrocene couple. IR compensation was achieved prior to each CV scan by measuring the uncompensated solution resistance followed by incremental compensation and circuit stability testing. Background CV scans of the electrolyte solution were recorded before adding the analytes. The half-wave potentials ($E_{1/2}$) were determined as averages of the cathodic and anodic peak potentials of reversible couples and are referenced to the external Fc^+/Fc couple.[28]

Electron Paramagnetic Resonance (EPR) was carried out on a 9. 6 GHz X-band Bruker EMXplus spectrometer with a dual mode cavity operating in perpendicular mode using an Oxford ESR900 continuous flow cryostat controlled with an Oxford ITC503S temperature controller. Spectra were acquired and baseline corrected using *Xenon* (v.1.1b.44). Simulations and fitting of spectra were carried out with *WinSim* (v.0.96).[29] The LMB1 and Simplex fitting algorithms were used as implemented in *WinSim*.

Compounds 2-amino-6-bromo-1,3-diethoxycarbonylazulene[30], bis(2-amino-1,3-diethoxycarbonyl-6-azulenyl)acetylene (**III.2a**)[31], bis(2-formamido-1,3-diethoxycarbonyl-6-azulenyl)acetylene (**III.2b**)[31], and $[(OC)_5W]_2(\mu$-**III.1c**$)$[9] were prepared according to literature procedures. Other reagents were obtained from commercial sources and used as received.

Synthesis of 2,2'-diamino-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl (III.1a).

A 100 mL side-arm round bottom flask (SARB) equipped with a Teflon-coated magnetic stir-bar and a reflux condenser was charged with $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (dppf = bis(diphenylphosphino)-ferrocene) (0.023 g, 0.028 mmol, Strem Chemicals Inc.), bis(pinacolato)diboron (0.018 g, 0.071 mmol), potassium acetate (0.087g, 0.886 mmol), and 2-amino-6-bromo-1,3-diethoxycarbonylazulene (0.100 g, 0.273 mmol). To this solid mixture, 30 mL of O_2- and H_2O-free DMSO was added via cannula. The resulting deep orange solution was stirred at 105 °C for 5 hours while gradually acquiring dark red-brown color. Then, the reaction mixture was cooled to room temperature and quenched with 20 mL of deionized water. The content of the flask was transferred into a 500 mL separatory funnel and diluted with additional 100 mL of H_2O. The mixture was extracted with CH_2Cl_2 (4×50 mL) until the dichloromethane extract was very pale orange. The aqueous layer progressively lost its red-orange color during extractions to become essentially colorless. Care was taken to avoid collecting a black film/suspension ("Pd-black"?) accumulating at the interface of the organic and aqueous layers. The organic extracts were combined, washed thoroughly with deionized water (3×200 mL) to remove any remaining DMSO, and dried over anhydrous Na_2SO_4. The drying agent was then filtered off and washed with a minimum amount of CH_2Cl_2. TLC of the filtrate (silica, hexanes/ethyl acetate 2:1) indicated practically clean formation of one product (R_f = 0.423) as well absence of starting material (R_f = 0.615). The filtrate was concentrated to about 15 mL (until the first crystals appeared), layered with 50 mL of pentane, and kept at -35 °C for 13 hours. A brick-red precipitate formed that was filtered-off, washed with pentane (4×25 mL), and dried at 0.005 Torr for 30 min to afford **III.1a** (0.071 g, 0.124 mmol) as a sparking brick-red powder in a 91% yield. The product was of sufficient purity to use in the next step. For larger scale

syntheses of **III.1a**, a recrystallization of the product from CH_2Cl_2/pentane was warranted on occasion to remove trace amounts of impurities, but any flash chromatographic manipulations with **III.1a** should be avoided. Mp: darkens at 152 °C and gradually decomposes above *ca.* 190 °C without clear melting. While the ^{1}H and ^{13}C NMR spectra of **III.1a** described herein are essentially identical to those described in the original report of this compound[23], the melting point of 298 °C (dec) previously reported[23] for **III.1a** appears to be unusually high for this type of compound.[20-22] MS (ES, positive m/z): calcd for $C_{32}H_{33}N_2O_8$ (M+1), 573.2; found, 573.2. ^{1}H NMR ($CDCl_3$, 400 MHz, 22°C): δ 1.51 (t, 3H, C*H*$_3$, $^{3}J_{HH}$ = 8 Hz), 4.50 (q, 2H, C*H*$_2$, $^{3}J_{HH}$ = 8 Hz), 7.79 (d, 1H, $H^{5,5',7,7'}$, $^{3}J_{HH}$ = 10 Hz), 7.88 (s, 1H, N*H*$_2$), 9.17 (d, 1H, $H^{4,4',8,8'}$, $^{3}J_{HH}$ = 10 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 22°C): δ 14.68 (*C*H_3), 59.96 (*C*H_2), 100.42, 130.49, 133.34, 144.92, 148.38 (aromatic C), 162.77 (*C*O_2Et), 166.47 (aromatic *C*) ppm. UV-vis (CH_2Cl_2, 22 °C): λ_{max} (log ε) 459 nm (4.51), 358 nm (4.79), 250 nm (4.71).

Synthesis of 2,2'-diformamido-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl (III.1b).

A mixture of acetic anhydride (9.90 mL, 0.105 mol) and formic acid (7.92 mL, 0.210 mol) was heated at 60°C for 2.5 hrs with stirring. To the resulting in situ formed acetic-formic anhydride, a solution of **III.1a** (0.600 g, 1.05 mmol) in a minimum amount of CH_2Cl_2 was added, along with additional formic acid (7.92 mL, 0.210 mol). The dark red reaction mixture was stirred at 60 °C for 18 hrs while gradually turning chestnut in color. Then the mixture was cooled to room temperature, quenched with 10% aqueous Na_2CO_3, and extracted with CH_2Cl_2 (3x100 mL). The dichloromethane extracts were combined, washed with 100 mL of deionized H_2O, and dried over anhydrous Na_2SO_4. The chestnut-colored solution was filtered to remove the drying agent and the filtrate was concentrated on a rotary evaporator. Addition of pentane to

the concentrated solution precipitated chestnut-colored solid, which was filtered off and dried *in vacuo* to afford **III.1b** (0.519 g, 0.826 mmol) in a 79% yield. Mp: 254-256 °C (dec). HRMS (ES, postive m/z): calcd for $C_{34}H_{33}N_2O_{10}$ (M+1), 629.2135; found, 629.2139. Anal. Calcd for $C_{34}H_{32}N_2O_{10}$: C, 64.96; H, 5.13; N, 4.46 (Calcd for $C_{34}H_{32}N_2O_{10}\cdot(CH_2Cl_2)_{0.47}$: C, 61.93; H, 4.97; N, 4.19). Found: C, 61.93; H, 4.56; N, 4.13. The presence of residual CH_2Cl_2 solvent in the sample of **III.1b** subjected to the elemental analysis was confirmed by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, 22°C): δ 1.49 (t, 6H, C*H*$_3$, $^3J_{HH}$ = 7 Hz), 4.52 (q, 4H, C*H*$_2$, $^3J_{HH}$ = 7 Hz), 7.95 (d, 2H, H$^{5,5',7,7'}$, $^3J_{HH}$ = 10 Hz), 8.70 (s, br, 1H, N*H*), 9.49 (d, 2H, H$^{4,4',8,8'}$, $^3J_{HH}$ = 10 Hz), 10.39 (s, br, 1H, C*H*O) ppm. UV-vis (CH_2Cl_2, 22 °C): λ_{max} (log ε) 474 nm (3.86), 421 nm (4.23), 368 nm (4.35 shoulder), 340 nm (4.52), 266 nm (4.36), 253 nm (4.37).

Synthesis of 2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl (III.1c)

The conditions have been adapted from Hashmi, *et al.*[32] 2,2'-diformamido-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl, **III.1b** (0.428 g, 0.681 mmol) was added to a 250ml side-armed round bottom flask and brought under Ar. 100 mL of distilled CH_2Cl_2 was added and stirred at -70°C for 15 min. $POCl_3$ (0.38 mL, 4.08 mmol) was added dropwise via syringe. The solution was left to stir at -70°C for 30 min. Diisopropylamine (1.73 mL, 12.26 mmol) was added dropwise via syringe. The solution was left to stir slowly warming to room temperature overnight. The solution was quenched with 100mL of 10% Na_2CO_3 (aq.). The solution was filtered and rinsed with a minimum of DI H_2O and CH_2Cl_2. The solution was then extracted in a separatory funnel with CH_2Cl_2. The organic layer was washed with 3 x 100 mL DI H_2O. The organic layer was then dried with Na_2SO_4, and excess solvent was removed by Rota-vap. The residue was recrystallized with EtOAc layered on top of CH_2Cl_2 at -40°C overnight. The precipitate was filtered off and dried under vacuum. 2,2'-diisocyano-1,1',3,3'-

tetraethoxycarbonyl-6,6'-biazulenyl, **III.1c**, was isolated in a 98% yield (0.396 g, 0.666 mmol). Characterization by ^{1}H, ^{13}C NMR and FTIR matches prior reported spectrum.[9] Mp: 225°C (dec). FTIR (CH_2Cl_2): ν_{CN} = 2127 cm^{-1}. FTIR (Nujol mull): ν_{CN} = 2130 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 22°C): δ 1.54 (t, 12H, CH_3, $^{3}J_{HH}$ = 8 Hz), 4.55 (q, 8H, CH_2, $^{3}J_{HH}$ = 8 Hz), 8.03 (d, 4H, $H^{5,5',7,7'}$, $^{3}J_{HH}$ = 10 Hz), 9.93 (d, 4H, $H^{4,4',8,8'}$, $^{3}J_{HH}$ = 10 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 22°C): δ 14.2 (CH_3), 61.3 (CH_2), 113.7, 131.9, 132.4, 140.2, 140.6, 156.5 (aromatic *C*), 163.1 (CO_2Et), 178.6 (*C*NR) ppm. ^{14}N NMR ($CDCl_3$, 36.2 MHz, 25°C): δ 172.85 (C*N*R) ppm. UV-vis (CH_2Cl_2, 22 °C): λ_{max} (log ε) 509 nm (3.48), 390 nm (4.48), 363 nm (4.72), 342 nm (4.80), 279 nm (4.48), 246 nm (4.60).

EPR of 2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl radical anion [III.1c]$^{-\cdot}$

In an inert atmosphere dry box, 2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl, **III.1c** (5 mg, 0.008 mmol) was added to decamethylcobaltocene (1 mg, 0.003mmol) in an Erlenmeyer flask. This was dissolved in 5 mL CH_2Cl_2 or THF and left to mix for 10 min. at 25°C. A small aliquot was transferred to an EPR tube and sealed with a plastic cap and Parafilm. The spectrum was taken at 201 K within 2 hours of preparing the sample. EPR acquisition parameters: attenuation = 26 dB, microwave power = 0.502 mW, frequency = 9.64 GHz, sweep width = 66.5 G, modulation amplitude = 0.100 G, modulation frequency = 100 kHz, gain = 45 dB, conversion time = 1.51 ms, time constant = 1.28 ms, and resolution = 6,650 points. Fitted hyperfine couplings in Gauss [in MHz]: 1.62 [4.54] ($H^{4,4',8,8'}$), 0.96 [2.69] ($H^{5,5',7,7'}$), 0.45 [1.26] (4 x CH_2), 0.41 [1.15] (2 x ^{14}N), line width = 0.061 G (reported couplings above are for CH_2Cl_2, but THF fitted couplings are within ±0.07 G).

UV-Vis-NIR studies of III.1c, $[III.1c]^{-}\cdot$ and $III.1c^{-2}$

In an inert atmosphere dry box, 5 mL of a $2.43x10^{-5}$ M THF or CH_3CN solution of 2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl, **III.1c** was added to 0.03 mL of a $2.13x10^{-3}$ M solution of decamethylcobaltocene in the same solvent to form **$[III.1c]^{-}\cdot$**. The sample was added to an air-free cuvette and the spectrum was recorded within 30 min. of generation. UV-Vis-NIR (THF, 22 °C): λ_{max} (log ε) 1064 nm (3.93), 951 nm (3.92), 629 nm (4.31), 344 nm (4.33). UV-Vis-NIR (CH_3CN, 22 °C): λ_{max} (log ε) 1044 nm (3.98), 944 nm (3.97), 621 nm (4.32), 341 nm (4.31).

The same procedure was used above to generate **$III.1c^{2-}$**, except the amount of the decamethylcobaltocene solution used was doubled to 0.06 mL. UV-Vis-NIR (THF, 22 °C): λ_{max} (log ε) 626 nm [sh] (3.42), 486 nm (4.26).

Synthesis of 1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl (III.1d)

The conditions have been adapted from McDonald, *et al.*[33] 2,2'-diamino-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl, **III.1a** (0.200 g, 0.349 mmol) and p-hydroxyquinone (0.077 g, 0.699 mmol) were added to a 500 mL 3-necked flask open to air. Concentrated H_2SO_4 (0.173 g, 1.70 mmol) was added to 10 mL of THF and 50 mL of 1,4-dioxane. This solution was added to the 3-necked flask and stirred. Addition funnel #1 contained isoamyl nitrite (1.88 mL, 14.0 mmol) in 35 mL of 1,4-dioxane. Addition funnel #2 contained p-hydroxyquinone (1.54 g, 14.0 mmol) in 35 mL of 1,4-dioxane. At room temperature with vigorous stirring, both addition funnels were simultaneously opened at a dropwise rate. After the addition, the solution was left to stir for 3 hours. The solution was quenched with 200 mL of 1M Na_2SO_3. The solution was extracted with a separatory funnel using CH_2Cl_2. The organic layer was washed 3 x 200 mL DI H_2O, dried with Na_2SO_4, and excess solvent was removed via Rota-vap. The residue was

recrystallized with pentane layered on top of CH_2Cl_2 at -40°C overnight. 1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl, **III.1d** was isolated in a 51% yield (0.096 g, 0.177 mmol). ^1H & ^{13}C NMR and UV-Vis compare favorably with prior literature.[34] Mp shows decomposition at 175°C, while the lit. value is 227.5 – 230°C. ^1H NMR ($CDCl_3$, 400 MHz, 22°C) δ 1.49 (t, 12H, CH_3, $^3J_{HH}$= 7 Hz), 4.48 (d, 8H, CH_2, $^3J_{HH}$ = 7 Hz), 7.97 (d, 4H, $H^{5,5',7,7'}$, $^3J_{HH}$ = 11 Hz), 8.92 (s, 2H, $H^{2,2'}$), 9.89 (d, 4H, $H^{4,4',8,8'}$, $^3J_{HH}$ = 11 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 22°C) δ 14.7 (CH_3), 60.5 (CH_2), 117.5, 131.4, 138.6, 143.1, 144.6, 156.0 (aromatic *C*), 165.0 (CO_2Et) ppm. UV-Vis (CH_2Cl_2, 22 °C) λ_{max}(log ε): 376 nm (4.50), 341 nm (4.61), 272 nm (4.41), 241 nm (4.58). MS (FAB+, m-nitrobenzyl alcohol): calc. for $C_{32}H_{30}O_8$ $(M+1)^+$, 543.2; found, 543.7.

Synthesis of bis(2-isocyano-1,3-diethoxycarbonyl-6-azulenyl)acetylene (III.2c)

The conditions have been adapted from Hashmi, *et al.*[32] bis(2-formamido-1,3-diethoxycarbonyl-6-azulenyl)acetylene, **III.2b** (0.125 g, 0.19 mmol) was added to a 250ml side-armed round bottom flask and brought under Ar. 100 mL of distilled CH_2Cl_2 was added and stirred at -70°C for 15 min. $POCl_3$ (0.11 mL, 1.18 mmol) was added dropwise via syringe. The solution was left to stir at -70°C for 30 min. Diisopropylamine (0.47 mL, 3.34 mmol) was added dropwise via syringe. The solution was left to stir slowly warming to room temperature overnight. The solution was quenched with 100mL of 10% Na_2CO_3 (aq.). The solution was filtered and rinsed with a minimum of DI H_2O and CH_2Cl_2. The solution was then extracted in a separatory funnel with CH_2Cl_2. The organic layer was washed with 3 x 100 mL DI H_2O. The organic layer was then dried with Na_2SO_4, and excess solvent was removed by Rota-vap. The residue was recrystallized with EtOAc layered on top of CH_2Cl_2 at -40°C overnight. The precipitate was filtered off and dried under vacuum. bis(2-isocyano-1,3-diethoxycarbonyl-6-azulenyl)acetylene, **III.2c** was isolated in a 97% yield (0.114 g, 0.18 mmol). Spectroscopic

characterizations were identical to that of the prior report of the compound.[31] FTIR (CH_2Cl_2): ν_{CN} = 2124 cm^{-1}; ν_{alkyne} = 2189 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C) δ 1.54 (t, 12H, CH_3, $^3J_{HH}$ = 7 Hz), 4.54 (q, 8H, CH_2, $^3J_{HH}$ = 7 Hz), 8.05 (d, 4H, $H^{5,5',7,7'}$, $^3J_{HH}$ = 11 Hz), 9.78 (d, 4H, $H^{4,4',8,8'}$, $^3J_{HH}$ = 11 Hz) ppm. ^{13}C{^{1}H } NMR ($CDCl_3$, 125.7 MHz, 25°C) δ 14.3 (*C*H_3), 61.4 (*C*H_2), 98.2 (*alkyne C atoms*), 113.9, 131.9, 134.7, 136.1, 139.4, 141.3 (*aromatic C*), 163.2 (*C*O_2R), 178.9 (*C*NR) ppm. UV-Vis (CH_2Cl_2, 22 °C) λ_{max}(log ε): 555 nm (3.80), 444 nm (4.76), 417 nm (4.68), 344 nm (4.79), 244 nm (4.76).

EPR of bis(2-isocyano-1,3-diethoxycarbonyl-6-azulenyl)acetylene radical anion [III.2c]$^-$·

In an inert atmosphere dry box, bis(2-isocyano-1,3-diethoxycarbonyl-6-azulenyl)acetylene, **III.2c** (5.6 mg, 0.009 mmol) was added to decamethylcobaltocene (1 mg, 0.003 mmol) in an Erlenmeyer flask. This was dissolved in 5 mL CH_2Cl_2 and left to mix for 10 min. at 25°C. A small aliquot was transferred to an EPR tube and sealed with a plastic cap and Parafilm. The spectrum was taken at 203 K within 2 hours of preparing the sample. EPR acquisition parameters: attenuation = 30 dB, microwave power = 0.200 mW, frequency = 9.63 GHz, sweep width = 66.5 G, modulation amplitude = 0.100 G, modulation frequency = 100 kHz, gain = 30 dB, conversion time = 1.53 ms, time constant = 0.64 ms, and resolution = 6,650 points. Fitted hyperfine couplings in Gauss [in MHz]: 1.36 [3.81] ($H^{4,4',8,8'}$), 1.08 [3.03] ($H^{5,5',7,7'}$), 0.89 [2.49] (4 x CH_2), 0.51 [1.43] (2 x ^{14}N), & line width = 0.03 G.

UV-Vis-NIR studies of III.2c, [III.2c]$^-$·, and III.2c^{2-}

In an inert atmosphere dry box, 5 mL of a 2.34x10^{-5} M THF solution of bis(2-isocyano-1,3-diethoxycarbonyl-6-azulenyl)acetylene, **III.2c** was added to 0.039 mL of a 2.98x10^{-3} M solution of decamethylcobaltocene in THF to form **[III.2c]$^-$·**. The sample was added to an air-free cuvette, and the spectrum was recorded within 30 min. of generation. UV-Vis-NIR (THF,

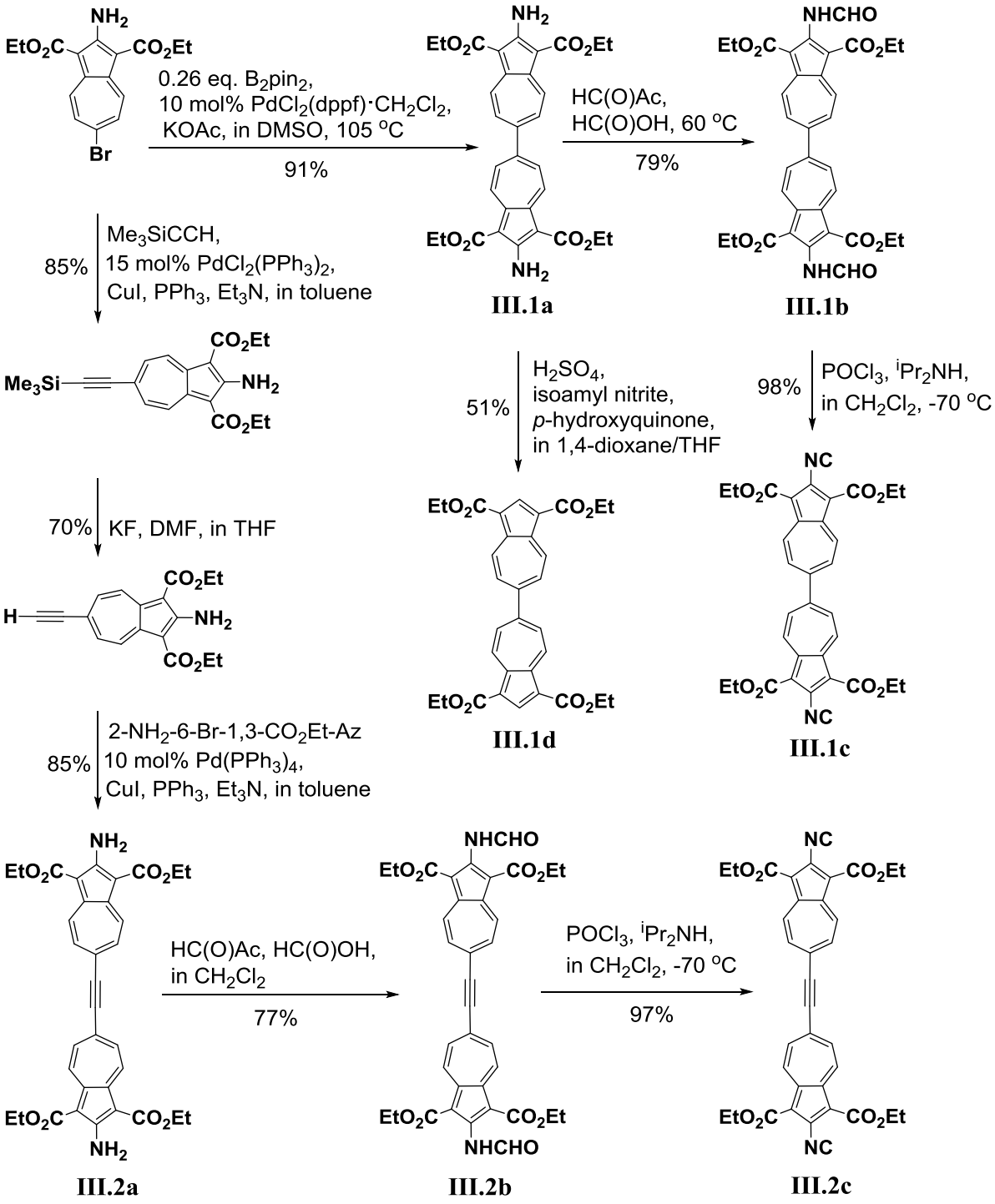
22 °C): λ_{max} (log ε) 1254 nm (4.92), 1106 nm (4.22), 1053 nm (4.13), 987 nm (3.96), 690 nm (4.77), 607 nm (4.47).

The same procedure was used above to generate **III.2c**$^{2-}$, except the amount of the decamethylcobaltocene solution used was doubled to 0.078 mL. UV-Vis-NIR (THF, 22 °C): λ_{max} (log ε) 603 nm (4.66), 568 nm (4.55), 497 nm (4.49).

Density Functional Theory calculations

Density functional theory (DFT) calculations on **[III.1c]**$^{-}$· and **[III.2c]**$^{-}$· were performed using the *ORCA* (v3.0) program.[35] All other DFT calculations on truncated models (designated with the ‘ symbol) were performed using the *ORCA* (v2.8.0) program.[36] Geometric optimizations and time-dependent DFT (TD-DFT) calculations were performed using the B3LYP functional with a TZVP basis set, the resolution of identity approximation (RI) ‘chain of spheres’ algorithm (RIJCOSX), and a SV/J auxiliary basis set [Ahlrich’s Coulomb fitting basis for split valence basis set with polarization (SVP)].[37-43] The B3LYP functional was chosen to calculate the total energies for its proven accuracy in organic systems.[44] Singlet states were calculated spin-restricted, while doublet and triplet states were spin-unrestricted. The solvation effects of dichloromethane (CH_2Cl_2) [ε = 9.08] were modeled using the conductor-like screening model (COSMO), as implemented in *ORCA*.[45] Solvated systems were again geometrically optimized using the aforementioned parameters. EPR hyperfine coupling parameters were computed as implemented in *ORCA*. Orbital surface contour plots were produced using the *Molekel* (v.5.4.0.8) program with isodensity values set at ±0.05 for Kohn-Sham orbitals and ±0.00001 for spin density plots.[46] The final Cartesian coordinates for all gas-phase optimized structures are in Appendix 3, Tables A3.1 – A3.29. Analysis of the TD-DFT calculations is presented in Appendix 3, Tables A3.30 – A3.35.

Results and Discussion



Scheme 3: Synthetic scheme for accessing compounds **III.1a-d** and **III.2a-c**.[9,31]

Combining the 6-bromoazulene derivative 2-amino-6-bromo-1,3-diethoxycarbonylazulene[30] with bis(pinacolato)diboron (B_2pin_2) in the presence of Pd(dppf)Cl_2 (dppf = bis(diphenylphosphino)ferrocene) under the conditions specified in Scheme 3 afforded brick-red 2,2-diamino-6,6'-biazulenyl **III.1a** in a 91% yield. Surprisingly, the best yields of this unexpected, "one-pot" homocoupling were achieved by employing a substoichiometric amount (*ca.* $^1/_4$ equiv) of B_2pin_2, see Table 1. No formation of **III.1a** was observed when the reaction was conducted in the absence of B_2pin_2 under otherwise identical conditions, but did afford 0.07 g of an orange-brown mixture, a significant component of which was identified as de-brominated starting material by ^{1}H NMR. Interestingly, our attempts to use $^1/_2$ equiv of B_2pin_2 (the stochiometric quantity of B_2pin_2 typically employed in one-pot homocoupling of organohalides via sequential Miyaura borylation / Suzuki cross-coupling)[47,48] invariably led to much lower yields (≤ 37%) of **III.1a**. Notably, the aqueous layer remaining after the CH_2Cl_2 extractions of the quenched reaction mixture had significant orange-brown color while the final dichloromethane extracts were practically colorless. The above quite efficient protocol for the preparation of **III.1a** evolved from our initial efforts to improve its original synthesis by Mutafuji, Sugihara *et al*.[23] The latter involved a Pd(dppf)Cl_2-catalyzed borylation of 2-amino-6-bromo-1,3-diethoxycarbonylazulene with 1.1 equiv of B_2pin_2 to isolate the corresponding 6-azulenyl-boronic ester, which was then cross-coupled with 2-amino-6-bromo-1,3-diethoxycarbonylazulene using a different catalyst, Pd(PPh_3)$_2Cl_2$, to give **III.1a** in a 17% overall yield.[23]

Table 1: Optimization of the number of equivalents of bis(pina-colato)diboron (B_2pin_2) used in the synthesis of **III.1a**. (Relative to 1 eq. of 2-amino-6-bromo-1,3-diethoxycarbonylazulene)

Equivalents of B_2pin_2	**III.1a Yield (%)**
0.26	91
0.55	37
0.10	16
0.00	0

Synthesis of **III.2a** was accomplished via a two-step Sonogashira cross-coupling.[31] Formylation of **III.1a** with acetic-formic anhydride afforded a 79% yield of sparingly soluble chestnut-colored 2,2'-diformamido-6,6'-biazulenyl **III.1b**, double dehydration of which gave lavender needles of 2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl **III.1c** in a 98% isolated yield. A similar formylation and dehydration scheme was used to produce **III.2b**[31] and **III.2c**. The FTIR and ^{13}C NMR spectra of **III.1c** exhibit signature peaks at $\nu_{C\equiv N}$ = 2130 cm^{-1} (in Nujol mull) and δ = 178.6 ppm (in $CDCl_3$), respectively, that correspond to the isocyanide termini of this air-stable compound. ^{14}N NMR was additionally taken of **III.1c**, in which the isocyanide gave a signal at 173 ppm, in line with other 2-isocyano-azulenyls.[49]

It is well-argued that varying the nature of a substituent and the position of its attachment permits tuning the $S_0 \rightarrow S_1$ excitation wavelength for substituted azulenes.[7] We found that the λ_{max} value for the relatively weak $S_0 \rightarrow S_1$ transition in the electronic spectra of **III.1a**, **III.1b**, and **III.1c** in CH_2Cl_2 appears to increase upon proceeding from **III.1a** to **III.1b** (474 nm) to **III.1c** (509 nm). For **III.1a**, the $S_0 \rightarrow S_1$ band is likely obscured by the lower energy tail of the

substantially more intense $S_0 \rightarrow S_2$ transition at λ_{max} = 459 nm. This trend nicely parallels the order of decreasing electron-donating / increasing-electron withdrawing strength of the substituents at the 2- and 2'-positions in these 6,6'-biazulenyls: $-NH_2$ > -NHCHO > -N≡C. At the same time, however, λ_{max} of the substantially more intense $S_0 \rightarrow S_2$ band increases in the reverse order **III.1c** (390 nm) < **III.1b** (421 nm) < **III.1a** (459 nm) and enters the visible region for **III.1a** and **III.1b**. Thus, the 2,2'-substitution of the 6,6'-biazulenyl scaffold provides a unique opportunity to simultaneously tune the wavelengths of both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations in mutually opposing directions.

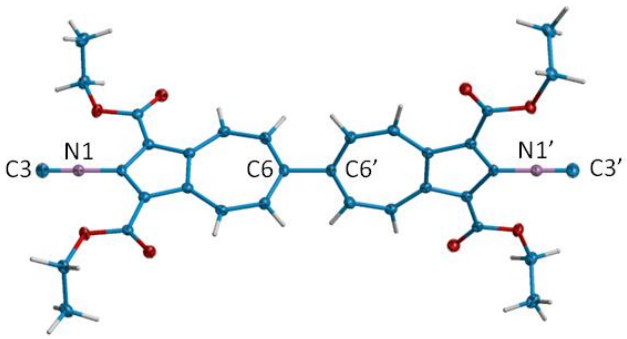


Figure 1: Molecular structure of **III.1c** (50% thermal ellipsoids).[9]

The solid state structure of **III.1c** depicted in Figure 1 is remarkably symmetric with only ¼ of the molecule being crystallographically independent. The C3-N1 bond length of 1.165(3) Å observed for **III.1c** is typical for an isocyano N≡C triple bond.[19] Every carboxylate unit in **III.1c** is essentially coplanar with the azulenic moiety to which it is attached. The long axis of **III.1c** spans 17.1 Å, as defined by the C3···C3' distance. The C6-C6' bond connecting the azulenyl rings in **III.1c** is 1.512(4) Å long. This distance is statistically shorter than the $C(sp^3)$-$C(sp^3)$ bond of 1.535(4) Å connecting the two 7-membered rings in 1,1',6,6'-tetrahydro-6,6'-biazulene-1,1'-diide, $[H_8C_{10}\text{-}C_{10}H_8]^{2-}$,[50] but only marginally longer than the central C-C bond

length documented for biphenyl (1.494(3) Å - 1.507 Å).[51,52] The 66.9° torsion angle between the azulenic planes in crystalline **III.1c** is almost certainly significantly influenced by crystal packing forces.

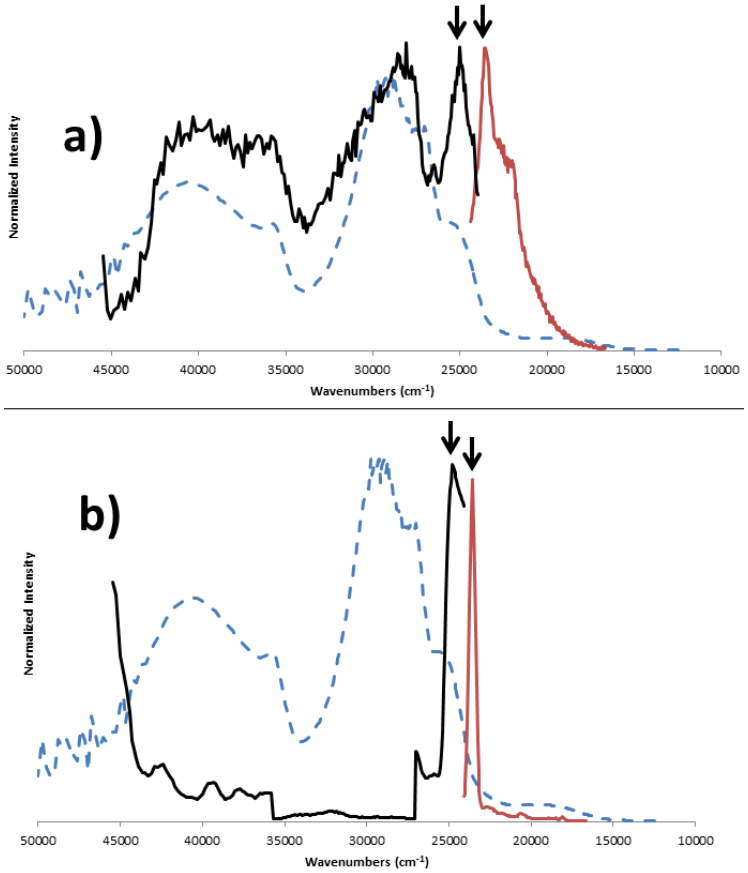


Figure 2: Fluorescence spectra of **III.1c** at 293 K in CH_2Cl_2 (a) and at 77 K in 2-MeTHF (b). [black arrows indicate maximum excitation ($\lambda_{Ex.}$) and emission ($\lambda_{Em.}$) peaks, blue dashed line is the UV-Vis absorption spectrum (in CH_2Cl_2 at 293 K), black solid line is the excitation spectrum, red solid line is the emission spectrum]

While there is plenty of literature precedents for the anti-Kasha fluorescence patterns of azulenic derivatives (see Chapter 1), no such characterization had been carried out upon biazulenyl systems (regardless of connectivity). Our preliminary assessment of the photoluminescence properties of biazulenyls were undertaken with **III.1c**, see Figure 2. At 293 K, the maximum excitation (Ex.) and emission (Em.) were λ_{Ex} = 25,000 cm^{-1} and λ_{Em} = 23,588

cm^{-1}, with a Stokes shift of 1,412 cm^{-1}. At 77 K, the maximum excitation (Ex.) and emission (Em.) were λ_{Ex} = 24,812 cm^{-1} and λ_{Em} = 23,588 cm^{-1}, with a Stokes shift of 1,224 cm^{-1}. Compared against the corresponding overlaid absorption spectrum, the excitation/emission measurements at both temperatures suggest the same conclusion that the emission arises from the second singlet excited state (S_2), which is in line with the anti-Kasha behaviour demonstrated for other azulenes. No phosphorescence was detected, which differs from other mono-azulene systems studied, see Chapter 1 of this work.

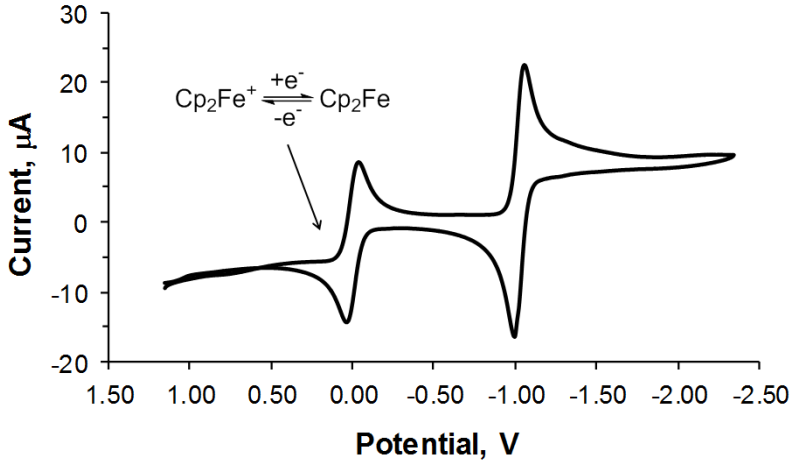
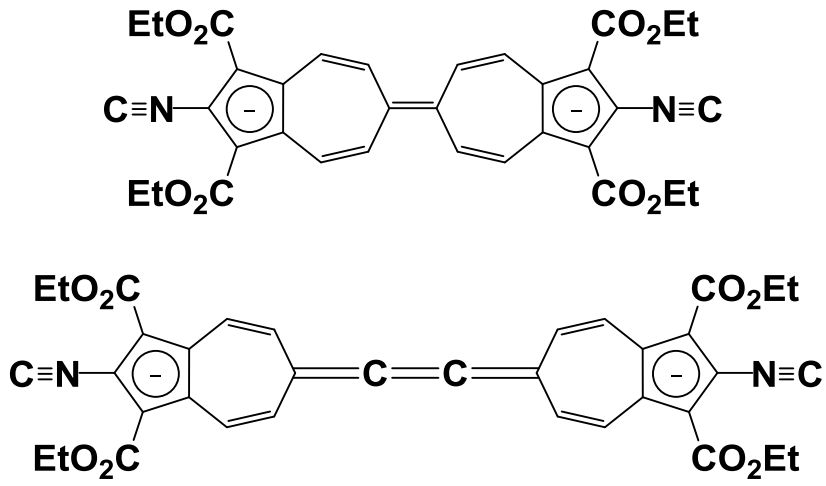


Figure 3: Cyclic voltammogram of **III.1c** in 0.1 M [$^{n}Bu_4N$][PF_6]/CH_2Cl_2 vs. internal Cp_2Fe^{+}/Cp_2Fe (1 equiv) at 25 °C. Scan rate = 100 mV. [Reprinted with permission. Copyright 2010 American Chemical Society.][9]

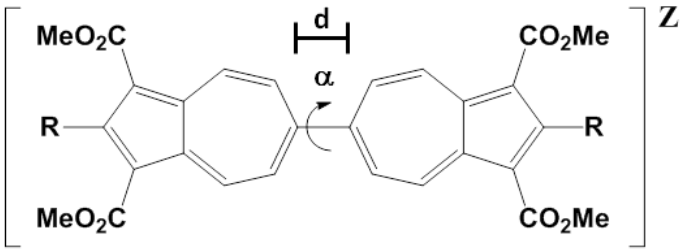


Scheme 4: Bis(cyclopentadienide)-like resonance forms of **III.1c**$^{2-}$ (top) and **III.2c**$^{2-}$ (bottom) [Reprinted with permission. Copyright 2010 American Chemical Society.][9]

2-isocyano-1,3-diethoxycarbonyl-azulene, the structure of which may be viewed as one-half of that of **III.1c**, undergoes an irreversible one-electron reduction at $E_{p,c}$ = -1.55 V vs. Cp_2Fe^+/Cp_2Fe in CH_2Cl_2. In sharp contrast, the cyclic voltammogram (CV) of **III.1c** in the same solvent features a nicely reversible ($i_{p,c}/i_{p,a}$ = 1.0) two-electron reduction wave at the substantially less negative potential of $E_{1/2}$ = -1.02 V (Figure 3). The CV for **III.2c** looks remarkably similar to that of **III.1c** except there are two, one-electron reductions at $E_{1/2}$ = -0.98 and -1.06 V, which were resolved using Differential Pulse Voltammetry (DPV).[31] The persistence of **III.1c**$^{2-}$ and **III.2c**$^{2-}$, at least on the electrochemical time scale, can be attributed to the closed-shell nature of its 6,6'-biazulenide dianion framework (Scheme 4).[53-56] The singlet electronic configuration of **III.1c**$^{2-}$ and **III.2c**$^{2-}$ is also suggested by the DFT examination of its model, *vide infra*.

The molecule of **III.1c** can be readily used to bridge metal centers. For example, treatment of *in situ*-generated $W(CO)_5(THF)$ with ½ equiv of **III.1c** in THF provided fuchsia-colored $[(OC)_5W]_2$(μ-**III.1c**) that features two "$(OC)_5W$" units linked through the 6,6'-biazulenyl bridge by means of the N≡C junctions. Complex $[(OC)_5W]_2$(μ-**III.1c**) undergoes a reversible

reduction at $E_{1/2}$ = -1.01 V in CH_2Cl_2. This reduction potential is almost identical to that of **III.1c** thereby indicating that the LUMO of $[(OC)_5W]_2$(μ-**III.1c**) is largely bridge-based. The lowest energy band (λ_{max} = 496 nm) in the electronic spectrum of $[(OC)_5W]_2$(μ-**III.1c**) can be assigned to the metal-to-bridge charge transfer (MBCT) and its molar extinction coefficient (ε) is *ca.* 35 times greater than that documented for the $S_0 \rightarrow S_1$ transition for **III.1c**. Notably, the analogous MBCT for $[(OC)_5W]_2$(μ-2,6-diisocyano-1,3-diethoxycarbonylazulene) has λ_{max} value of 515 nm,[19] whereas the corresponding transition for $[(OC)_5W]_2$(μ-1,4-diisocyanobenzene) occurs in the UV region (λ_{max} = 370 nm).[57]

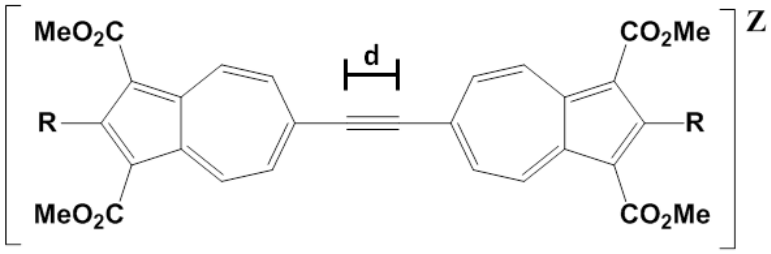


Scheme 5: Truncated model system used in the calculations for **III.1a-d'**, where Z is the charge of the molecule, *d* is the bond distance between the azulene rings, and α is the torsional angle between the azulene ring planes, see also Table 2.

Table 2: DFT computed geometry optimizations for the series **III.1a-d'** in various redox states, see also Scheme 5. The lowest energy state for the dianion was also determined, where S = singlet state and T = triplet state.

-R	**Z**	**ΔE_{gas}(eV)**	**ΔE_{CH2Cl2}(eV)**	**α (°)**	***d* (Å)**
-NH_2 III.1a'	0	0	0	45.94	1.497
	-1	-	-	29.33	1.458
	-2 (S)	-0.46	-4.90	16.97	1.418
	-2 (T)	0.14	-4.41	28.28	1.475
-NHCHO III.1b'	0	0	0	48.34	1.500
	-1	-	-	31.07	1.459
	-2 (S)	-1.64	-5.70	17.17	1.418

	-2 (T)	-0.86	-5.02	53.13	1.501
-NC III.1c'	0	0	0	49.61	1.499
	-1	-	-	30.88	1.460
	-2 (S)	-2.53	-6.38	19.03	1.419
	-2 (T)	-1.79	-5.75	49.41	1.502
-H III.1d'	0	0	0	50.16	1.502
	-1	-	-	31.77	1.460
	-2 (S)	-1.47	-5.89	19.34	1.417
	-2 (T)	-0.65	-5.07	69.19	1.507



Scheme 6: Truncated model system used in the calculations for **III.2a-c'**, where Z is the charge of the molecule and *d* is the bond distance between the acetylene bridged carbons, see also Table 3.

Table 3: DFT computed geometry optimizations for the series **III.2a-c'** in various redox states, see also Scheme 6. The lowest energy state for the dianion was also determined, where S = singlet state and T = triplet state.

-R	**Z (Charge)**	**ΔE_{gas}(eV)**	**$\Delta E_{CH_2Cl_2}$(eV)**	***d* (Å)**
-NH_2 III.2a'	0	0	0	1.212
	-1	-	-	1.226
	-2 (S)	-1.08	-5.40	1.244
	-2 (T)	-0.43	-4.74	1.224
-NHCHO III.2b'	0	0	0	1.211
	-1	-	-	1.226
	-2 (S)	-2.2	-6.16	1.244
	-2 (T)	-1.58	-5.56	1.223
-NC III.2c'	0	0	0	1.211
	-1	-	-	1.225
	-2 (S)	-3.04	-6.83	1.243
	-2 (T)	-2.38	-6.14	1.217

In order to probe whether the singlet or triplet state is favored for the ground state of the dianions, density functional theory (DFT) was employed utilizing *ORCA*.[36] In the Barybin group's prior communication, a similar study was done using a model compound (2,2'-diisocyano-6,6'-biazulenyl with no ethoxycarbonyl groups).[9] Because the ethoxycarbonyl groups do contribute to the HOMO of the system, we wanted to reprobe the calculations using a truncated model system of methoxycarbonyl groups (designated compounds **III.1c'** and **III.2c'**) shown in Tables 2 and 3. This new truncated model would preserve the electronic effects on the biazulenic core. The compounds were optimized in the gas phase (B3LYP / TZVP) with the methoxycarbonyl groups in the same orientation as the X-ray crystal structure of **III.1c**.[9] Clearly the singlet state is energetically favored by 17 kcal/mol (**III.1c'**) and 15 kcal/mol (**III.2c'**). Condensed phase modelling in CH_2Cl_2 correlated well with the gas phase determinations. These patterns were seen for all the rest of the series studied **III.1a,b,d**' and **III.2a,b'**.

Table 2 also shows an interesting progression both in terms of the interplanar torsion angle and the bond distance between the azulenyl rings. The torsional angle shifts in **III.1a-d** from the neutral of *ca.* 50° to the dianion (S) of *ca.* 25°, indicating greater double bond character between the azulene rings in the singlet state dianion. This trend is complemented by the bond distance shrinking from 1.49 to 1.41 Å. A similar progression can be seen for the **III.2a-c** family in that the distance of the acetylene bridge (*d*) lengthens as the reduction occurs, likely moving from a triply bonded to a doubly bonded bridge. Also interesting is the **III.1c**$^{2-}$ triplet state parameters more closely resemble the neutral species, predicting a single bond between the azulene rings. The monoanion geometric parameters fit nicely midway of **III.1c** and **III.1c**$^{2-}$ (S), indicating a resonance structure in between a single and double bond. This

theoretical analysis complements a prior report on the EPR of the 6,6'-biazaulenyl radical anion.[58]

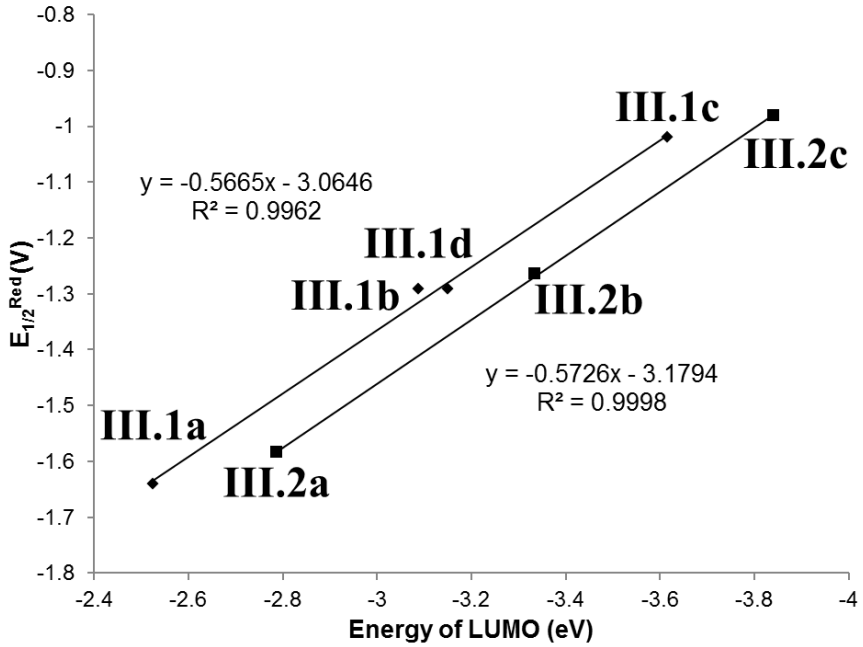
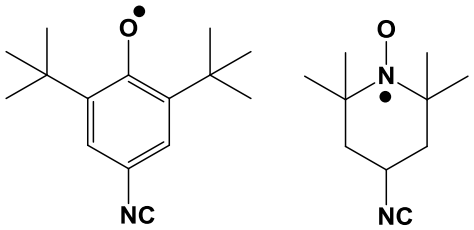


Figure 4: Correlation of the DFT predicted LUMO energy level with the experimentally determined $E_{1/2}$ reduction potential.

An interesting relationship is clearly evident when the LUMO of the biazulenyls (**III.1a-d**, **III.2a-c**) is compared to the $E_{1/2}$ reduction potentials, Figure 4. This strong correlation can be reasoned by relating the LUMO of the system to electron affinity by Koopmans' theorem, which was originally applied to correlating the HOMO with the ionization potential.[59] The cyclic voltammetry experiments are a direct probe of the electron affinity through the determination of the reversible reduction potential. The power of this correlation allows for the accurate prediction from DFT of the electronics by substitution at the 2,2' positions in the biazulenyl scaffold. Figure 4 is also quite reminiscent of other linear-free energy relationships such as the classic physical organic example of the Hammett Plot.[60]



Scheme 7: The only two documented organic radicals featuring isocyanides.[27,28]

To further explore the reduced states of the biazulenyl systems, electron paramagnetic resonance (EPR) was employed, Figures 5 and 6. Very few azulene based systems have been characterized by EPR due to the generally unstable nature of organic radicals.[61] Additionally, there are only two examples of organic radicals featuring isocyanide groups, see Scheme 7.[62,63] In order to generate the radical anion, decamethylcobaltocene ($CoCp^*_2$) ($E_{1/2}$ = -1.94 V vs. ferrocene)[28] was added to a three-fold excess of 6,6'-bizaulenyl (**III.1c** or **III.2c**) in CH_2Cl_2 or THF. Both the neutral biazulenyls and $[CoCp^*_2]^+$ are EPR silent, and $CoCp^*_2$ is EPR silent at 200K. This ensured the only signals present were due to the biazulenic radical anions. While the EPR spectra were taken within 2 hours of radical generation, the radicals seemed persistent for *ca.* 2 days at room temperature under argon, in line with a separate report on the related system 6,6'-biazulenyenide.[58]

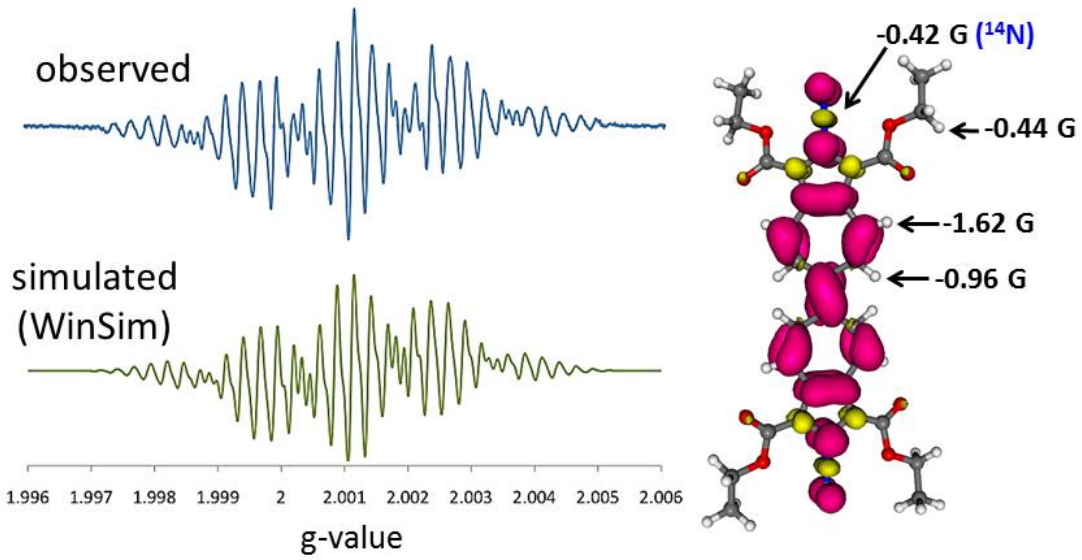


Figure 5: X-band EPR spectrum of **[III.1c]**$^{-\cdot}$ (top left) with the spectral simulation (bottom left). Right, DFT generated spin density of **[III.1c]**$^{-\cdot}$ with hyperfine couplings (from the spectral simulation) noted in Gauss.

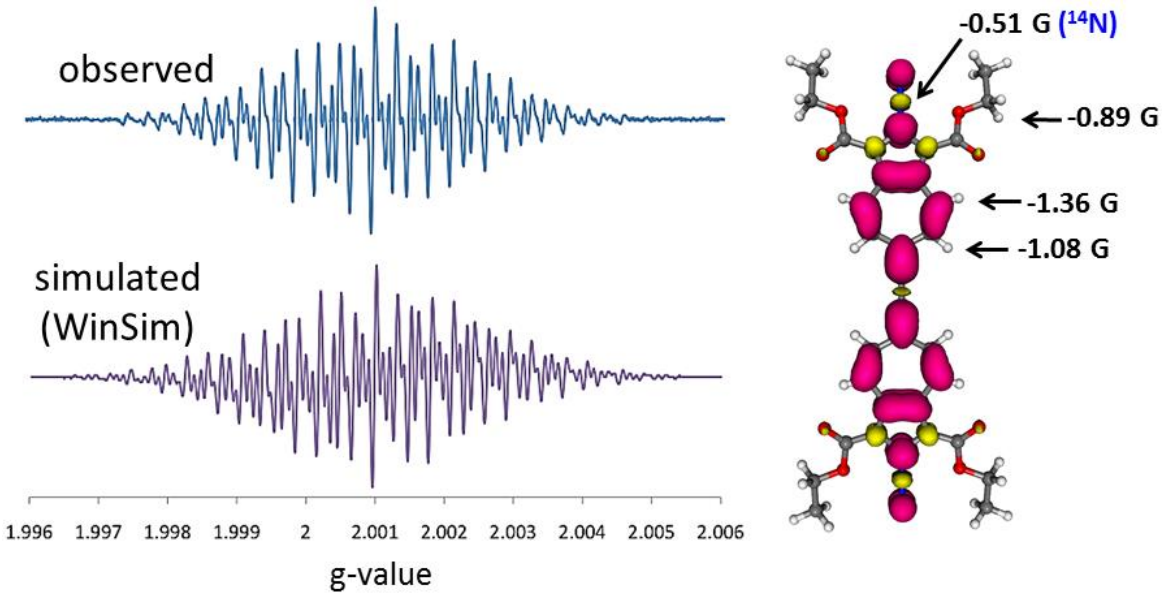


Figure 6: X-band EPR spectrum of **[III.2c]**$^{-\cdot}$ (top left) with the spectral simulation (bottom left). Right, DFT generated spin density of **[III.2c]**$^{-\cdot}$ with hyperfine couplings (from the spectral simulation) noted in Gauss.

Table 4: Compilation of the hyperfine couplings from spectral simulations and the corresponding DFT predictions of **[III.1c]$^{-}$·** and **[III.2c]$^{-}$·**, in Guass.

	Number	Nuclei	DFT Predicted	Simulation
[III.1c]$^{-}$·	2	-^{14}N≡C	-0.97	-0.42
	4	*H* (4,4',8,8')	-2.16	-1.62
	4	*H* (5,5',7,7')	-0.40	-0.96
	8	-CH_2-	-0.07	-0.44
[III.2c]$^{-}$·	2	-^{14}N≡C	-0.90	-0.51
	4	*H* (4,4',8,8')	-1.84	-1.36
	4	*H* (5,5',7,7')	-0.65	-1.08
	8	-CH_2-	-0.07	-0.89

The experimental spectra were than simulated and fitted using *WinSim*.[29] Hyperfine coupling constants are reported in Table 4. Initial simulation parameters were obtained from the EPR of 6,6'-bizaulenyenide.[58] Accurate simulations required full delocalization throughout the biazulenic core. Attempts to simulate the system using the radical localized on one azulenyl ring were inaccurate descriptions. As expected, a McConnell-type relation[61,64] was observed when the aromatic hydrogen hyperfine couplings were compared with the singly-occupied molecular orbital (SOMO), Figure 7, or the spin density plot of the radical anions, shown in Figures 5 and 6. The DFT generated spin density plots assign all of the hyperfine couplings as negative values. What was initially surprising was the need to include the four –CH_2- moieties from the ethoxycarbonyl groups in the simulation, but there is precedence in analogous methoxycarbonylpyridinyl radicals.[65,66] No enhancement of the simulation was evidenced by the inclusion of the –CH_3 moieties from the ethoxycarbonyl groups.

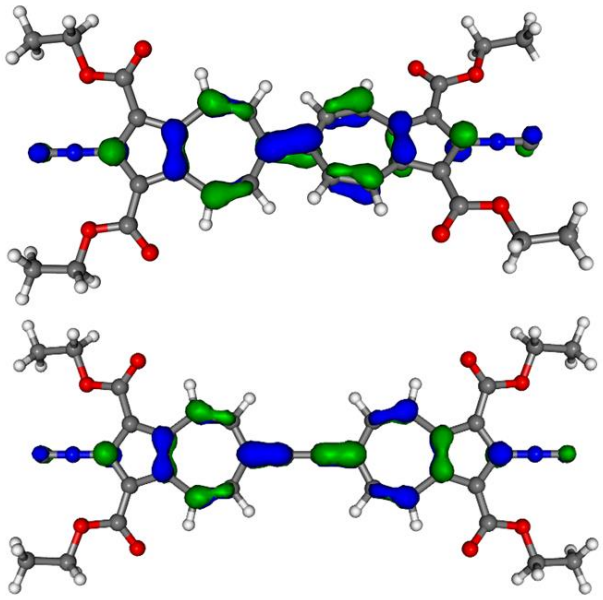


Figure 7: DFT generated SOMO diagrams of **[III.1c]$^{-\cdot}$** (top) and **[III.2c]$^{-\cdot}$** (bottom).

Between both radical anions (**[III.1c]$^{-\cdot}$** and **[III.2c]$^{-\cdot}$**), the ^{14}N (nuclear spin = 1) hyperfine coupling of the isocyanide moieties are similar (0.42 G and 0.51 G respectively) and constitutes the first such report in nearly 50 years, likely due to the tendency for radical isocyanides to polymerize.[67] The only other known ^{14}N hyperfine coupling is of a neutral radical isocyanide is 5.0 G (Scheme 7, left).[62] Another report consists of a nitroxide radical where there is no observed ^{14}N hyperfine coupling due to localization of the radical on the N-O bond (Scheme 7, right).[63]

To experimentally probe if the triplet state is formed upon reduction to the dianion, a sample of neutral ligand (**III.1c**) was added to 2.1 equivalents of $CoCp^*_2$ in THF. Both perpendicular and parallel modes showed only background signal at 200K. This provides experimental support with the prediction from the DFT calculations, *vide supra*, indicating only the singlet state dianion is formed.

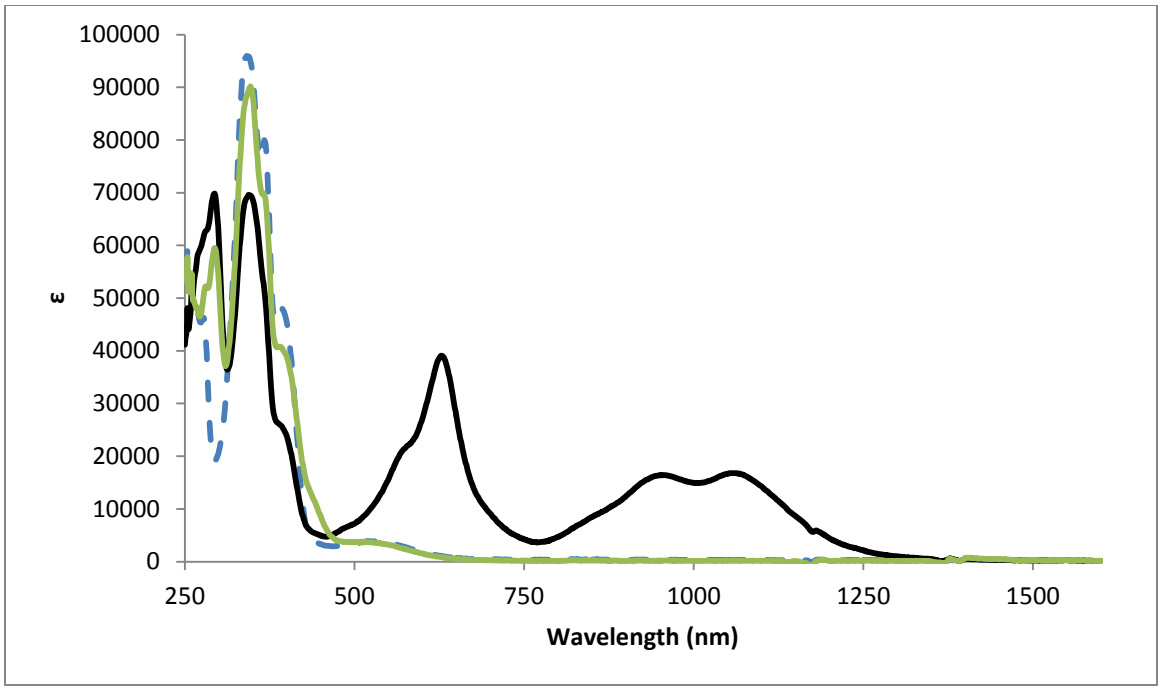


Figure 8: UV-Vis-NIR spectra in THF at 24°C of **III.1c** (blue dashed), with 1 eq. of $CoCp_2^*$ added (black solid), and following that, 1 eq. of $NO(BF_4)$ added (green solid).

While the CV measurements clearly indicate the reversibility of the two-electron process for **III.1c**, the one-electron process was unresolved. To determine the reversibility of the one-electron process, UV-Vis-NIR measurements were employed using chemical reduction and subsequent oxidation. An initial spectrum of the neutral ligand was obtained, Figure 8 (blue dashed). After reduction with 1 eq. of $CoCp^*_2$ in THF, a sizable shift in the spectrum was evidenced, Figure 8 (black solid). The radical anion was then chemically oxidized back to the neutral state using 1 eq. of $NO(BF_4)$, which ensured minimal interference with the visible spectrum Figure 8 (green solid). The only significant deviations between the neutral and oxidized spectra are due to the $[CoCp^*_2][BF_4]$ complex in the UV region, indicating one-electron reversibility of the 6,6'-biazulenyl core.[68]

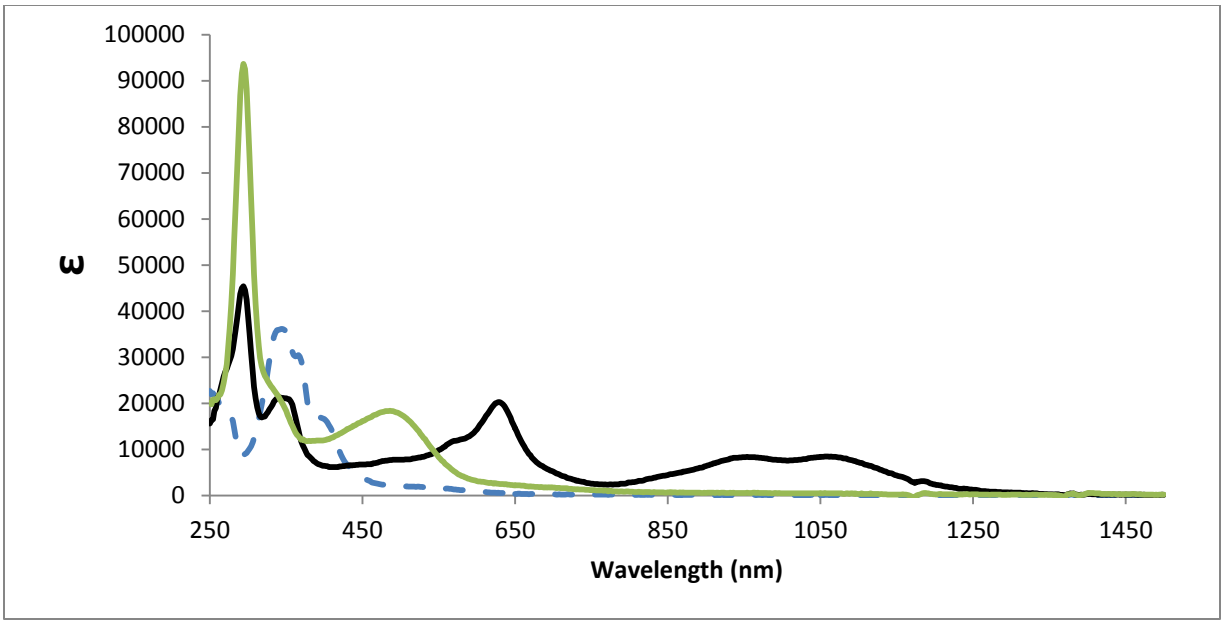


Figure 9: UV-Vis-NIR spectra in THF at 24°C of **III.1c** (blue dashed), **[III.1c]**$^{-}$**·** (black solid), **III.1c**$^{2-}$ (green solid).

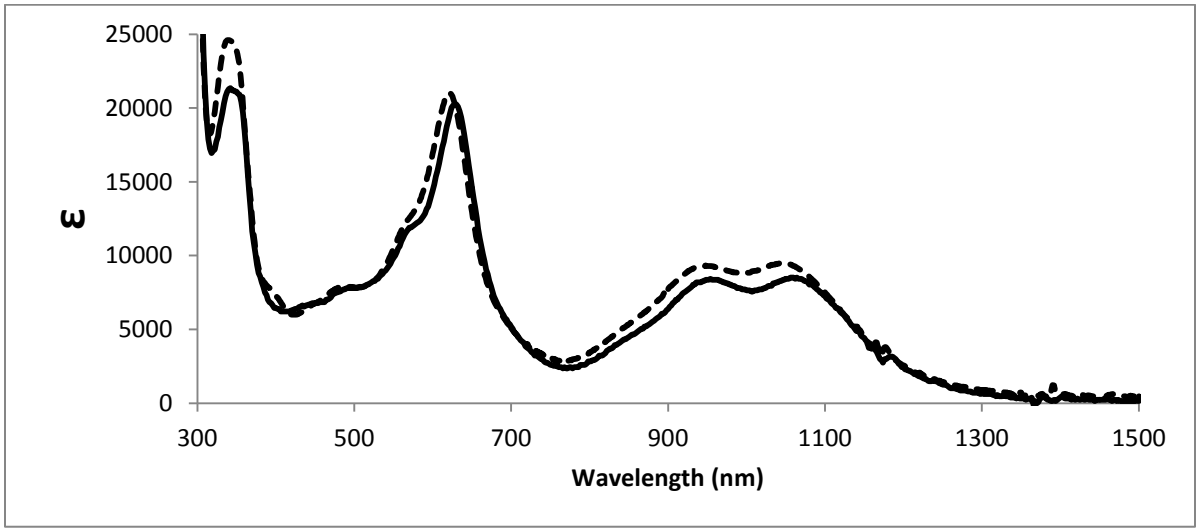


Figure 10: UV-Vis-NIR spectra in THF (solid) and CH_3CN (dashed) at 24°C of **[III.1c]**$^{-}$**·**.

Upon reduction of **III.1c** to the mono- and di-anions, large changes in solution color were observed. UV-Vis-NIR spectroscopy revealed likewise large changes between species, Figure 9. The S_0 to S_1 transition of the neutral species at 509 nm is washed out upon reduction to **[III.1c]**$^{-}$**·** by a sizeable peak at 626 nm and a broad doublet at 951 and 1064 nm. This NIR feature has been evidenced in other radical anion electronic spectra for azulenide and naphthalide.[69] If the

transition had charge-transfer character, than a change in solvent (which also had a corresponding change in the dielectric constant) would significantly shift the observed spectrum. As shown in Figure 10, the overlay of the spectra in THF (solid) and acetonitrile (dashed) [dielectric constants: THF = 7.52, CH_3CN = 36.64] shows almost no differences. TD-DFT suggests this is a SOMO→LUMO transition (Table A3.31), though the doublet-like feature is postulated to be an interference dip (Fano-type interference).[70] Upon further reduction to the dianion (**III.1c**$^{2-}$), the NIR feature recedes and a different feature grows in at 631 nm. Again, TD-DFT analysis suggests this is the HOMO→LUMO transition (Table A3.32). The LUMO of **III.1c** becomes the SOMO in **[III.1c]**$^{-}$**·** and the HOMO in **III.1c**$^{2-}$.

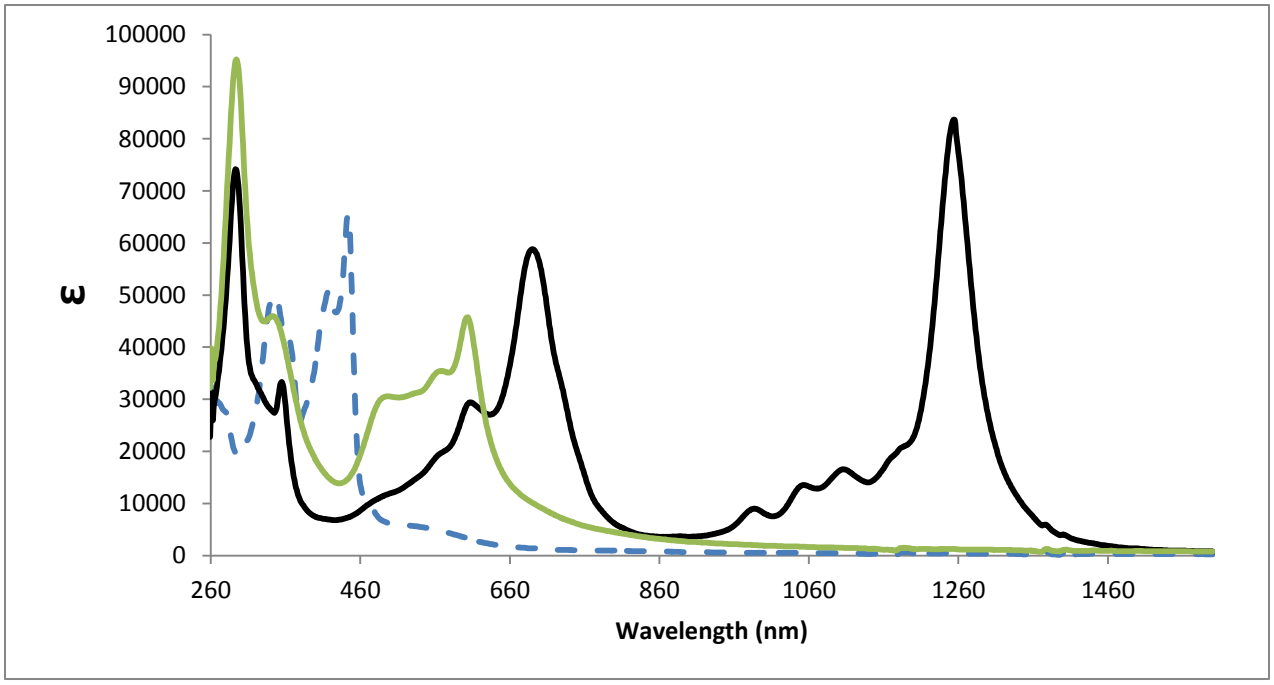


Figure 11: UV-Vis-NIR spectra in THF at 24°C of **III.2c** (blue dashed), **[III.2c]**$^{-}$**·** (black solid), **III.2c**$^{2-}$ (green solid).

To complement the UV-Vis-NIR studies on **III.1c**, a similar reduction scheme with $CoCp_2$* was employed to study **III.2c**, see Figure 11. Again, very large shifts in the spectra are

noted between **III.2c** (blue dashed), **[III.2c]$^{-}$·** (black solid), **III.2c^{-2}** (green solid). Of interest is the *ca.* 200 nm red-shift in the spectra vs. the **III.1c** series in Figure 9. As the acetylene bridge allows for better conjugation between the azulenyl rings, the spectra reflect this increased π-system in the form of a red-shift. The NIR feature at 1254 nm in **[III.2c]$^{-}$·** is much more intense than in **[III.1c]$^{-}$·** and seems to even show a vibronic coupling pattern at 1106, 1053, and 987 nm. TD-DFT suggests the NIR feature is a SOMO→LUMO transition (Table A3.34), while the absorption at 690 nm is primarily the SOMO-1→ SOMO transition. Upon further reduction to **III.2c^{2-}**, the NIR feature disappears while a band grows in at 603 nm. TD-DFT again suggests this is primarily a HOMO→LUMO transition (Table A3.35).

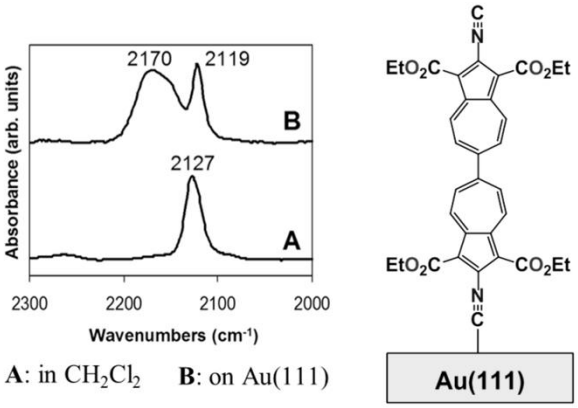


Figure 12: Right: schematic drawing of the terminal upright (η^1) bonding of **III.1c** to the gold surface. Left: $\nu_{C\equiv N}$ regions of (A) FTIR spectrum of **III.1c** in CH_2Cl_2 solution and (B) RAIR spectrum of a SAM film of **III.1c** on Au(111). [Reprinted with permission. Copyright 2010 American Chemical Society.][9]

Dr. Brad M. Neal and Dr. Tiffany R. Maher demonstrated that **III.1c** can form self-assembled monolayers on Au(111) with perfectly upright η^1 coordination of **III.1c** to the gold surface, see Figure 12.[9,27] The grazing incidence reflection absorption infrared (RAIR) spectrum of a freshly prepared film of **III.1c** on Au(111) also suggests the end-on adsorption of **III.1c** to the Au surface.

Conclusion and Future Work

In this Chapter, symmetric linear biazulenic pi-linkers featuring two isocyanide junction groups were introduced. The key step in the synthesis of the title scaffold **III.1c** involved an unexpected and remarkably efficient "one-pot" homo-coupling of a 6-bromoazulene derivative. The unusual two-electron reduction behavior of the 6,6'-biazulenyl moiety is topologically complementary to the two-electron oxidation of the substantially more prevalent 1,1'-biazulenyl motif. This comprehensive study provided a thorough understanding of the molecular and electronic structures, redox behavior, radical-anion EPR spectra, complexation, and self-assembly of the 2,2'-diisocyano-6,6'-biazulenyl motif and its analogue containing an ethynylene spacer between the azulenic moieties. Further efforts aimed at isolation and structural characterization of the radical anions and closed-shell dianions of **III.1c** and **III.2c** are currently underway. The diisocyanide-terminated biazulenic linkers **III.1c** and **III.2c** will be employed to assemble novel redox-adressable, azulene-based metal-organic frameworks. In addition, systematic conductivity studies of **III.1c** and **III.2c** self-assembled on metallic gold surfaces will be performed as well. In order to improve the packing quality of these molecular films, it may ultimately be necessary to develop syntheses of the analogues of **III.1c** and **III.2c** lacking the ester substituents at positions 1, 1', 3, and 3' of the biazulenic scaffold.

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Appendix 1. Supplementary Information for Chapter 1

Table A1.1. Sample and crystal data for I.2a.

Identification code	NG_823_MBar_OTT_113	
Chemical formula	$C_{34}H_{30}AuO_4PS$	
Formula weight	762.60	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.080 x 0.110 mm	
Crystal habit	Clear, light, red-orange block	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.7040(4) Å	α = 96.0340(10)°
	b = 10.3830(5) Å	β = 94.4100(10)°
	c = 16.6002(8) Å	γ = 90.2790(10)°
Volume	1487.36(12) $Å^3$	
Z	2	
Density (calculated)	1.703 g/cm^3	
Absorption coefficient	5.107 mm^{-1}	
F(000)	752	

Table A1.2. Data collection and structure refinement for I.2a.

Theta range for data collection	1.97 to 31.34°	
Index ranges	-12<=h<=12, -15<=k<=15, -24<=l<=24	
Reflections collected	23741	
Independent reflections	9555 [R(int) = 0.0298]	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9555 / 6 / 393	
Goodness-of-fit on F^2	1.257	
Δ/σ_{max}	0.001	
Final R indices	8041 data; I>2σ(I)	R1 = 0.0320, wR2 = 0.0527
	all data	R1 = 0.0463, wR2 = 0.0600
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0031P)^2+2.4617P]$	

	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.680 and -2.667 eÅ^{-3}
R.M.S. deviation from mean	0.219 eÅ^{-3}

Table A1.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for I.2a.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Au1	0.27001(2)	0.13333(2)	0.17639(2)	0.01628(4)
C1	0.4879(4)	0.0375(3)	0.3348(2)	0.0156(6)
C2	0.4680(4)	0.1600(3)	0.3785(2)	0.0165(7)
C3	0.5714(4)	0.1738(3)	0.4481(2)	0.0184(7)
C4	0.5875(4)	0.2856(3)	0.5030(2)	0.0237(8)
C5	0.6811(5)	0.3090(4)	0.5745(2)	0.0291(9)
C6	0.7827(5)	0.2254(4)	0.6104(2)	0.0315(9)
C7	0.8185(5)	0.0994(4)	0.5828(2)	0.0287(9)
C8	0.7637(4)	0.0230(4)	0.5125(2)	0.0226(8)
C9	0.6557(4)	0.0511(3)	0.4506(2)	0.0173(7)
C10	0.6029(4)	0.9699(3)	0.3795(2)	0.0160(7)
C11	0.3474(4)	0.2564(3)	0.3625(2)	0.0195(7)
C12	0.0769(4)	0.2889(4)	0.3469(3)	0.0323(10)
C13	0.9344(5)	0.2152(4)	0.3631(3)	0.0419(12)
C14	0.6551(4)	0.8399(3)	0.3518(2)	0.0178(7)
C15	0.7670(11)	0.6455(7)	0.3810(6)	0.024(2)
C16	0.8502(9)	0.5901(7)	0.4526(4)	0.0271(17)
C16A	0.7333(11)	0.5602(7)	0.4058(7)	0.047(2)
C15A	0.8309(10)	0.6687(8)	0.3838(8)	0.032(3)
C17	0.2441(4)	0.4282(3)	0.1045(2)	0.0168(7)
C18	0.2831(4)	0.4815(3)	0.0351(2)	0.0193(7)
C19	0.3639(4)	0.5991(3)	0.0429(2)	0.0229(8)
C20	0.4047(4)	0.6628(3)	0.1191(2)	0.0233(8)
C21	0.3648(4)	0.6101(3)	0.1882(2)	0.0231(8)
C22	0.2860(4)	0.4927(3)	0.1811(2)	0.0209(7)
C23	0.1216(4)	0.2142(3)	0.9921(2)	0.0181(7)
C24	0.9837(4)	0.2250(3)	0.9453(2)	0.0233(8)
C25	0.9741(4)	0.1864(4)	0.8624(2)	0.0289(9)
C26	0.1028(5)	0.1383(3)	0.8256(2)	0.0279(8)
C27	0.2402(4)	0.1270(4)	0.8717(2)	0.0268(8)

C28	0.2500(4)	0.1626(3)	0.9548(2)	0.0213(7)
C29	0.9527(4)	0.3100(3)	0.1305(2)	0.0199(7)
C30	0.9016(4)	0.4354(4)	0.1495(2)	0.0216(7)
C31	0.7568(4)	0.4556(4)	0.1788(2)	0.0263(8)
C32	0.6631(4)	0.3515(4)	0.1886(3)	0.0327(10)
C33	0.7119(4)	0.2270(4)	0.1687(3)	0.0376(11)
C34	0.8567(4)	0.2054(4)	0.1401(3)	0.0304(9)
O1	0.3714(3)	0.3695(2)	0.35529(16)	0.0275(6)
O2	0.2058(3)	0.2047(2)	0.36214(15)	0.0224(5)
O3	0.6218(3)	0.7828(2)	0.28585(16)	0.0275(6)
O4	0.7456(4)	0.7851(3)	0.40792(16)	0.0406(8)
P1	0.14435(10)	0.27345(8)	0.09916(6)	0.01708(18)
S1	0.39346(10)	0.97455(8)	0.24249(5)	0.01862(17)

Table A1.4. Bond lengths (Å) for I.2a.

Au1-P1	2.2690(9)	Au1-S1	2.3006(9)
C1-C2	1.414(4)	C1-C10	1.430(4)
C1-S1	1.745(3)	C2-C3	1.404(5)
C2-C11	1.482(5)	C3-C4	1.397(5)
C3-C9	1.476(5)	C4-C5	1.385(5)
C5-C6	1.387(6)	C6-C7	1.385(5)
C7-C8	1.391(5)	C8-C9	1.394(5)
C9-C10	1.420(5)	C10-C14	1.466(4)
C11-O1	1.212(4)	C11-O2	1.341(4)
C12-O2	1.449(4)	C12-C13	1.511(5)
C14-O3	1.203(4)	C14-O4	1.347(4)
C15-O4	1.488(7)	C15-C16	1.511(8)
C16A-C15A	1.500(8)	C15A-O4	1.458(7)
C17-C18	1.393(5)	C17-C22	1.394(5)
C17-P1	1.814(3)	C18-C19	1.396(5)
C19-C20	1.385(5)	C20-C21	1.388(5)
C21-C22	1.385(5)	C23-C24	1.390(5)
C23-C28	1.401(5)	C23-P1	1.814(4)
C24-C25	1.388(5)	C25-C26	1.387(5)
C26-C27	1.383(5)	C27-C28	1.385(5)
C29-C30	1.390(5)	C29-C34	1.397(5)
C29-P1	1.816(3)	C30-C31	1.394(5)
C31-C32	1.382(5)	C32-C33	1.378(6)

C33-C34	1.391(5)

Table A1.5. Bond angles (°) for I.2a.

P1-Au1-S1	173.70(3)	C2-C1-C10	108.1(3)
C2-C1-S1	127.9(3)	C10-C1-S1	124.1(2)
C3-C2-C1	109.4(3)	C3-C2-C11	122.5(3)
C1-C2-C11	127.8(3)	C4-C3-C2	124.5(3)
C4-C3-C9	128.2(3)	C2-C3-C9	107.3(3)
C5-C4-C3	129.6(4)	C4-C5-C6	128.4(4)
C7-C6-C5	128.8(4)	C6-C7-C8	129.8(4)
C7-C8-C9	129.8(4)	C8-C9-C10	128.0(3)
C8-C9-C3	125.3(3)	C10-C9-C3	106.7(3)
C9-C10-C1	108.5(3)	C9-C10-C14	128.2(3)
C1-C10-C14	123.3(3)	O1-C11-O2	123.5(3)
O1-C11-C2	125.1(3)	O2-C11-C2	111.3(3)
O2-C12-C13	106.2(3)	O3-C14-O4	120.8(3)
O3-C14-C10	125.1(3)	O4-C14-C10	114.1(3)
O4-C15-C16	105.6(6)	O4-C15A-C16A	104.1(6)
C18-C17-C22	119.8(3)	C18-C17-P1	122.0(3)
C22-C17-P1	118.1(3)	C17-C18-C19	119.6(3)
C20-C19-C18	120.2(3)	C19-C20-C21	120.1(3)
C22-C21-C20	120.0(3)	C21-C22-C17	120.2(3)
C24-C23-C28	119.3(3)	C24-C23-P1	122.1(3)
C28-C23-P1	118.5(3)	C25-C24-C23	120.3(3)
C26-C25-C24	120.1(4)	C27-C26-C25	119.9(4)
C26-C27-C28	120.3(3)	C27-C28-C23	120.0(3)
C30-C29-C34	119.3(3)	C30-C29-P1	123.3(3)
C34-C29-P1	117.3(3)	C29-C30-C31	120.0(3)
C32-C31-C30	120.3(4)	C33-C32-C31	120.0(4)
C32-C33-C34	120.3(4)	C33-C34-C29	120.1(4)
C11-O2-C12	116.9(3)	C14-O4-C15A	119.6(6)
C14-O4-C15	110.2(4)	C17-P1-C23	105.67(16)
C17-P1-C29	105.79(15)	C23-P1-C29	106.74(16)
C17-P1-Au1	112.47(11)	C23-P1-Au1	113.15(11)
C29-P1-Au1	112.46(12)	C1-S1-Au1	111.71(11)

Table A1.6. Torsion angles (°) for I.2a.

C10-C1-C2-C3	2.2(4)	S1-C1-C2-C3	-177.5(2)
C10-C1-C2-C11	-170.8(3)	S1-C1-C2-C11	9.5(5)
C1-C2-C3-C4	177.0(3)	C11-C2-C3-C4	-9.6(5)
C1-C2-C3-C9	-2.8(4)	C11-C2-C3-C9	170.6(3)
C2-C3-C4-C5	177.7(4)	C9-C3-C4-C5	-2.5(6)
C3-C4-C5-C6	-0.8(7)	C4-C5-C6-C7	1.8(7)
C5-C6-C7-C8	0.2(7)	C6-C7-C8-C9	-1.0(7)
C7-C8-C9-C10	180.0(4)	C7-C8-C9-C3	-1.2(6)
C4-C3-C9-C8	3.6(6)	C2-C3-C9-C8	-176.6(3)
C4-C3-C9-C10	-177.4(3)	C2-C3-C9-C10	2.4(4)
C8-C9-C10-C1	177.9(3)	C3-C9-C10-C1	-1.1(4)
C8-C9-C10-C14	-3.7(6)	C3-C9-C10-C14	177.4(3)
C2-C1-C10-C9	-0.6(4)	S1-C1-C10-C9	179.1(2)
C2-C1-C10-C14	-179.2(3)	S1-C1-C10-C14	0.6(5)
C3-C2-C11-O1	60.0(5)	C1-C2-C11-O1	-127.8(4)
C3-C2-C11-O2	-116.0(3)	C1-C2-C11-O2	56.2(4)
C9-C10-C14-O3	-169.1(3)	C1-C10-C14-O3	9.1(5)
C9-C10-C14-O4	11.7(5)	C1-C10-C14-O4	-170.1(3)
C22-C17-C18-C19	0.0(5)	P1-C17-C18-C19	-178.1(3)
C17-C18-C19-C20	-0.2(5)	C18-C19-C20-C21	-0.3(5)
C19-C20-C21-C22	0.9(5)	C20-C21-C22-C17	-1.2(5)
C18-C17-C22-C21	0.7(5)	P1-C17-C22-C21	178.9(3)
C28-C23-C24-C25	-0.7(5)	P1-C23-C24-C25	175.6(3)
C23-C24-C25-C26	-0.9(6)	C24-C25-C26-C27	1.0(6)
C25-C26-C27-C28	0.4(6)	C26-C27-C28-C23	-2.0(5)
C24-C23-C28-C27	2.1(5)	P1-C23-C28-C27	-174.4(3)
C34-C29-C30-C31	0.9(5)	P1-C29-C30-C31	-175.4(3)
C29-C30-C31-C32	-0.4(6)	C30-C31-C32-C33	-0.6(6)
C31-C32-C33-C34	1.2(7)	C32-C33-C34-C29	-0.8(7)
C30-C29-C34-C33	-0.3(6)	P1-C29-C34-C33	176.2(3)
O1-C11-O2-C12	4.1(5)	C2-C11-O2-C12	-179.8(3)
C13-C12-O2-C11	-171.1(3)	O3-C14-O4-C15A	13.4(6)
C10-C14-O4-C15A	-167.4(5)	O3-C14-O4-C15	-10.5(6)
C10-C14-O4-C15	168.8(5)	C16A-C15A-O4-C14	-98.2(8)
C16A-C15A-O4-C15	-26.4(13)	C16-C15-O4-C14	-172.3(6)
C16-C15-O4-C15A	69.3(17)	C18-C17-P1-C23	2.1(3)
C22-C17-P1-C23	-176.0(3)	C18-C17-P1-C29	-110.8(3)
C22-C17-P1-C29	71.1(3)	C18-C17-P1-Au1	126.0(3)
C22-C17-P1-Au1	-52.1(3)	C24-C23-P1-C17	-100.3(3)
C28-C23-P1-C17	76.0(3)	C24-C23-P1-C29	12.0(3)
C28-C23-P1-C29	-171.7(3)	C24-C23-P1-Au1	136.2(3)

C28-C23-P1-Au1	-47.5(3)	C30-C29-P1-C17	2.9(4)
C34-C29-P1-C17	-173.3(3)	C30-C29-P1-C23	-109.3(3)
C34-C29-P1-C23	74.4(3)	C30-C29-P1-Au1	126.1(3)
C34-C29-P1-Au1	-50.2(3)	C2-C1-S1-Au1	15.3(3)
C10-C1-S1-Au1	-164.4(2)		

Table A1.7. Anisotropic atomic displacement parameters (Å^2) for I.2a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	0.01413(6)	0.01348(6)	0.02152(7)	0.00281(4)	0.00187(4)	0.00183(4)
C1	0.0187(16)	0.0136(15)	0.0156(16)	0.0034(12)	0.0050(13)	-0.0010(12)
C2	0.0202(17)	0.0130(15)	0.0174(16)	0.0019(13)	0.0074(13)	0.0019(13)
C3	0.0227(17)	0.0135(16)	0.0203(17)	0.0010(13)	0.0105(14)	-0.0007(13)
C4	0.035(2)	0.0149(17)	0.0219(19)	0.0016(14)	0.0077(16)	-0.0025(15)
C5	0.046(2)	0.0203(19)	0.0208(19)	-0.0020(15)	0.0060(17)	-0.0058(17)
C6	0.043(2)	0.031(2)	0.0195(19)	0.0004(16)	-0.0008(17)	-0.0078(19)
C7	0.036(2)	0.029(2)	0.0216(19)	0.0065(16)	-0.0028(17)	-0.0022(17)
C8	0.0264(19)	0.0206(18)	0.0222(18)	0.0074(14)	0.0040(15)	0.0003(14)
C9	0.0207(17)	0.0141(16)	0.0184(17)	0.0047(13)	0.0057(13)	0.0006(13)
C10	0.0173(16)	0.0138(15)	0.0178(16)	0.0037(13)	0.0044(13)	0.0026(12)
C11	0.0261(18)	0.0169(17)	0.0158(17)	-0.0006(13)	0.0071(14)	0.0033(14)
C12	0.025(2)	0.024(2)	0.051(3)	0.0089(19)	0.0164(19)	0.0146(16)
C13	0.024(2)	0.043(3)	0.065(3)	0.019(2)	0.019(2)	0.0099(19)
C14	0.0167(16)	0.0148(16)	0.0222(18)	0.0021(13)	0.0036(14)	0.0011(13)
C15	0.025(5)	0.022(5)	0.024(4)	-0.002(4)	0.004(5)	0.020(4)
C16	0.036(4)	0.023(4)	0.024(4)	0.006(3)	0.003(3)	0.016(3)
C16A	0.050(6)	0.036(5)	0.058(7)	0.005(5)	0.019(5)	0.014(5)
C15A	0.021(5)	0.031(5)	0.043(6)	0.002(4)	0.004(5)	0.017(4)
C17	0.0123(15)	0.0135(15)	0.0249(18)	0.0029(13)	0.0013(13)	0.0030(12)
C18	0.0178(17)	0.0168(17)	0.0231(18)	0.0006(14)	0.0023(14)	0.0045(13)
C19	0.0237(18)	0.0178(17)	0.029(2)	0.0060(15)	0.0086(15)	0.0034(14)
C20	0.0174(17)	0.0158(17)	0.037(2)	0.0013(15)	0.0068(15)	-0.0005(13)
C21	0.0169(17)	0.0215(18)	0.030(2)	-0.0027(15)	0.0024(15)	0.0003(14)
C22	0.0173(17)	0.0237(18)	0.0225(18)	0.0039(14)	0.0041(14)	0.0003(14)
C23	0.0171(16)	0.0117(15)	0.0256(18)	0.0027(13)	0.0001(14)	0.0000(12)
C24	0.0180(17)	0.0219(18)	0.029(2)	-0.0012(15)	0.0000(15)	0.0035(14)
C25	0.026(2)	0.0230(19)	0.037(2)	0.0020(17)	-0.0069(17)	-0.0011(15)
C26	0.035(2)	0.0187(18)	0.029(2)	-0.0026(15)	0.0018(17)	-0.0072(16)

C27	0.0252(19)	0.0219(19)	0.033(2)	-0.0026(16)	0.0093(16)	-0.0015(15)
C28	0.0142(16)	0.0182(17)	0.031(2)	-0.0007(15)	0.0011(14)	-0.0003(13)
C29	0.0147(16)	0.0211(18)	0.0245(18)	0.0051(14)	0.0011(14)	0.0022(13)
C30	0.0186(17)	0.0242(19)	0.0220(18)	0.0042(15)	-0.0014(14)	0.0004(14)
C31	0.0246(19)	0.030(2)	0.024(2)	0.0010(16)	0.0007(15)	0.0122(16)
C32	0.0156(18)	0.046(3)	0.039(2)	0.013(2)	0.0068(17)	0.0068(17)
C33	0.0150(18)	0.039(2)	0.063(3)	0.018(2)	0.0128(19)	-0.0006(17)
C34	0.0180(18)	0.0210(19)	0.055(3)	0.0071(18)	0.0123(18)	0.0000(15)
O1	0.0328(15)	0.0130(12)	0.0379(16)	0.0052(11)	0.0057(12)	0.0023(11)
O2	0.0212(13)	0.0172(12)	0.0313(14)	0.0077(11)	0.0105(11)	0.0059(10)
O3	0.0303(15)	0.0202(13)	0.0296(15)	-0.0044(11)	-0.0037(12)	0.0093(11)
O4	0.066(2)	0.0302(16)	0.0246(15)	-0.0007(12)	-0.0026(14)	0.0329(15)
P1	0.0134(4)	0.0133(4)	0.0248(5)	0.0030(3)	0.0023(3)	0.0000(3)
S1	0.0212(4)	0.0134(4)	0.0204(4)	-0.0005(3)	-0.0010(3)	0.0031(3)

Table A1.8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for I.2a.

	x/a	y/b	z/c	U(eq)
H4	0.5249	0.3560	0.4893	0.028
H5	0.6750	0.3931	0.6025	0.035
H6	0.8346	0.2592	0.6606	0.038
H7	0.8916	0.0591	0.6172	0.034
H8	0.8064	-0.0611	0.5057	0.027
H12B	0.0740	0.3683	0.3774	0.039
H12A	0.0659	0.3073	0.2839	0.039
H13B	-0.0587	0.1970	0.4200	0.063
H13C	-0.0736	0.1335	0.3276	0.063
H13A	-0.1570	0.2673	0.3522	0.063
H15A	0.8290	-0.3649	0.3333	0.029
H15B	0.6661	-0.3987	0.3663	0.029
H16A	0.9430	-0.3578	0.4708	0.041
H16B	0.8794	-0.4994	0.4363	0.041
H16C	0.7822	-0.4085	0.4970	0.041
H16D	0.7194	-0.4275	0.4641	0.071
H16E	0.7841	-0.5225	0.3926	0.071
H16F	0.6325	-0.4401	0.3751	0.071
H15C	0.9340	-0.3297	0.4136	0.038
H15D	0.8436	-0.3400	0.3247	0.038
H18	0.2549	0.4380	-0.0172	0.023

H19	0.3911	0.6356	-0.0043	0.027
H20	0.4600	0.7427	0.1242	0.028
H21	0.3915	0.6546	0.2404	0.028
H22	0.2605	0.4561	0.2285	0.025
H24	-0.1043	0.2590	-0.0298	0.028
H25	-0.1208	0.1929	-0.1691	0.035
H26	0.0965	0.1132	-0.2313	0.034
H27	0.3284	0.0945	-0.1536	0.032
H28	0.3439	0.1520	-0.0135	0.026
H30	-0.0346	0.5072	0.1425	0.026
H31	-0.2776	0.5414	0.1920	0.032
H32	-0.4351	0.3658	0.2090	0.039
H33	-0.3535	0.1556	0.1745	0.045
H34	-0.1097	0.1193	0.1271	0.037

Table A1.9. Hydrogen bond distances (Å) and angles (°) for I.2a.

	Donor-H	**Acceptor-H**	**Donor-Acceptor**	**Angle**
C22-H22···O1	0.95	2.50	3.318(4)	143.9

Table A1.10. Sample and crystal data for I.2c.

Identification code	NG_824_MBar_OTT_60	
Chemical formula	$C_{34}H_{30}AuO_4PS$	
Formula weight	762.57	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal size	0.075 x 0.080 x 0.090 mm	
Crystal habit	clear light red-orange prism	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.8224(4) Å	α = 78.2800(10)°
	b = 12.6279(5) Å	β = 78.5020(10)°
	c = 14.0790(6) Å	γ = 73.7450(10)°
Volume	1457.39(11) $Å^3$	
Z	2	

Density (calculated)	1.738 g/cm^3
Absorption coefficient	5.212 mm^{-1}
F(000)	752

Theta range for data collection	1.49 to 31.00°
Index ranges	-12<=h<=12, -18<=k<=18, -20<=l<=20
Reflections collected	22943
Independent reflections	9143 [R(int) = 0.0385]
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	9143 / 6 / 380
Goodness-of-fit on F^2	1.286
Final R indices	7303 data; I>2σ(I) R1 = 0.0382, wR2 = 0.0628
	all data R1 = 0.0613, wR2 = 0.0767
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0083P)^2+3.1994P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.086 and -2.990 eÅ^{-3}
R.M.S. deviation from mean	0.271 eÅ^{-3}

Table A1.11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for I.2c.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Au1	0.83130(2)	0.44857(2)	0.11800(2)	0.01775(5)
C1	0.3918(5)	0.0935(3)	0.9195(3)	0.0166(9)
C2	0.5357(5)	0.0975(3)	0.8568(3)	0.0157(9)
C3	0.6025(5)	0.1743(3)	0.8859(3)	0.0147(8)
C4	0.7507(5)	0.1973(4)	0.8474(3)	0.0185(9)
C5	0.8273(5)	0.2647(4)	0.8759(3)	0.0200(9)
C6	0.7738(5)	0.3371(4)	0.9460(3)	0.0169(9)
C7	0.6212(5)	0.3586(4)	0.0016(3)	0.0202(10)
C8	0.4987(5)	0.3071(4)	0.0122(3)	0.0184(9)
C9	0.4887(5)	0.2213(4)	0.9667(3)	0.0165(9)
C10	0.3615(5)	0.1678(4)	0.9857(3)	0.0159(9)
C11	0.2263(5)	0.1812(3)	0.0663(3)	0.0152(9)
C12	0.9880(5)	0.1261(4)	0.1387(4)	0.0238(10)
C13	0.8862(6)	0.0600(4)	0.1162(4)	0.0252(11)

	x/a	y/b	z/c	U(eq)
C14	0.6034(5)	0.0338(4)	0.7759(3)	0.0197(9)
C17	0.7443(5)	0.5823(4)	0.3229(3)	0.0160(9)
C18	0.7637(6)	0.5727(4)	0.4206(3)	0.0255(11)
C19	0.7839(6)	0.6630(4)	0.4551(4)	0.0294(11)
C20	0.7868(6)	0.7616(4)	0.3925(4)	0.0274(10)
C21	0.7662(6)	0.7719(4)	0.2962(4)	0.0262(11)
C22	0.7459(5)	0.6827(4)	0.2609(3)	0.0204(10)
C23	0.7796(5)	0.3424(4)	0.3620(3)	0.0180(9)
C24	0.9305(5)	0.2721(4)	0.3446(3)	0.0214(10)
C25	0.9787(6)	0.1771(4)	0.4116(4)	0.0272(11)
C26	0.8762(6)	0.1520(4)	0.4963(4)	0.0270(11)
C27	0.7253(6)	0.2205(4)	0.5134(4)	0.0306(12)
C28	0.6764(6)	0.3152(4)	0.4468(4)	0.0263(11)
C29	0.5034(5)	0.4874(4)	0.2850(3)	0.0186(9)
C30	0.4486(6)	0.4139(4)	0.2468(3)	0.0243(10)
C31	0.2873(6)	0.4235(5)	0.2537(4)	0.0303(12)
C32	0.1788(6)	0.5070(5)	0.2995(4)	0.0318(12)
C33	0.2305(6)	0.5802(4)	0.3372(4)	0.0299(12)
C34	0.3939(5)	0.5710(4)	0.3297(3)	0.0229(10)
O1	0.2074(4)	0.2354(3)	0.1315(2)	0.0241(7)
O2	0.1226(4)	0.1227(3)	0.0600(2)	0.0211(7)
O3	0.7297(4)	0.0343(3)	0.7218(2)	0.0260(8)
O4	0.5051(4)	0.9738(3)	0.7651(2)	0.0330(9)
P1	0.71793(13)	0.46723(10)	0.27396(8)	0.0164(2)
S1	0.91453(14)	0.40588(10)	0.96010(8)	0.0224(3)
C16A	0.4257(12)	0.8904(10)	0.6526(8)	0.044(3)
C15A	0.5639(9)	0.9201(9)	0.6777(6)	0.0274(10)
C15	0.5599(13)	0.8861(6)	0.7047(5)	0.0238(10)
C16	0.5251(17)	0.9410(10)	0.6036(5)	0.045(4)

Table A1.12. Bond lengths (Å) for I.2c.

Au1-P1	2.2538(11)	Au1-S1	2.3208(12)
C1-C10	1.392(6)	C1-C2	1.402(6)
C1-H47	0.95	C2-C3	1.427(6)
C2-C14	1.460(6)	C3-C4	1.398(6)
C3-C9	1.463(6)	C4-C5	1.382(6)
C4-H52	0.95	C5-C6	1.405(6)

C5-H53	0.95	C6-C7	1.400(6)
C6-S1	1.762(4)	C7-C8	1.380(6)
C7-H43	0.95	C8-C9	1.396(6)
C8-H42	0.95	C9-C10	1.421(6)
C10-C11	1.470(6)	C11-O1	1.212(5)
C11-O2	1.352(5)	C12-O2	1.451(5)
C12-C13	1.497(6)	C12-H7	1.0989
C12-H8	1.0989	C13-H44	0.98
C13-H45	0.98	C13-H46	0.98
C14-O3	1.219(5)	C14-O4	1.348(5)
C17-C22	1.387(6)	C17-C18	1.397(6)
C17-P1	1.817(4)	C18-C19	1.393(7)
C18-H30	0.95	C19-C20	1.375(7)
C19-H29	0.95	C20-C21	1.379(7)
C20-H26	0.95	C21-C22	1.386(6)
C21-H28	0.95	C22-H27	0.95
C23-C24	1.384(6)	C23-C28	1.397(6)
C23-P1	1.820(5)	C24-C25	1.387(6)
C24-H41	0.95	C25-C26	1.384(7)
C25-H40	0.95	C26-C27	1.375(7)
C26-H39	0.95	C27-C28	1.382(7)
C27-H38	0.95	C28-H28A	0.95
C29-C34	1.379(6)	C29-C30	1.393(6)
C29-P1	1.817(4)	C30-C31	1.380(6)
C30-H35	0.95	C31-C32	1.381(7)
C31-H34	0.95	C32-C33	1.371(7)
C32-H33	0.95	C33-C34	1.397(6)
C33-H32	0.95	C34-H31	0.95
O4-C15	1.450(5)	O4-C15A	1.460(5)
C16A-C15A	1.494(5)	C16A-H16A	0.98
C16A-H16B	0.98	C16A-H16C	0.98
C15A-H15A	0.99	C15A-H15B	0.99
C15-C16	1.502(5)	C15-H15C	0.99
C15-H15D	0.99	C16-H16D	0.98
C16-H16E	0.98	C16-H16F	0.98

Table A1.13. Bond angles (°) for I.2c.

P1-Au1-S1	168.49(4)	C10-C1-C2	109.9(4)
C10-C1-H47	125.1	C2-C1-H47	125.1
C1-C2-C3	108.0(4)	C1-C2-C14	125.4(4)

C3-C2-C14	126.6(4)	C4-C3-C2	126.7(4)
C4-C3-C9	126.5(4)	C2-C3-C9	106.7(4)
C5-C4-C3	129.9(4)	C5-C4-H52	115.0
C3-C4-H52	115.0	C4-C5-C6	130.4(4)
C4-C5-H53	114.8	C6-C5-H53	114.8
C7-C6-C5	125.3(4)	C7-C6-S1	119.8(3)
C5-C6-S1	115.0(3)	C8-C7-C6	130.5(4)
C8-C7-H43	114.7	C6-C7-H43	114.7
C7-C8-C9	129.9(4)	C7-C8-H42	115.1
C9-C8-H42	115.1	C8-C9-C10	126.6(4)
C8-C9-C3	126.4(4)	C10-C9-C3	106.8(4)
C1-C10-C9	108.5(4)	C1-C10-C11	125.0(4)
C9-C10-C11	126.3(4)	O1-C11-O2	122.8(4)
O1-C11-C10	126.2(4)	O2-C11-C10	111.0(4)
O2-C12-C13	107.0(4)	O2-C12-H7	110.6
C13-C12-H7	116.3	O2-C12-H8	110.1
C13-C12-H8	117.5	H7-C12-H8	95.0
C12-C13-H44	109.5	C12-C13-H45	109.5
H44-C13-H45	109.5	C12-C13-H46	109.5
H44-C13-H46	109.5	H45-C13-H46	109.5
O3-C14-O4	122.3(4)	O3-C14-C2	126.4(4)
O4-C14-C2	111.2(4)	C22-C17-C18	119.1(4)
C22-C17-P1	118.8(3)	C18-C17-P1	122.1(3)
C19-C18-C17	120.3(4)	C19-C18-H30	119.9
C17-C18-H30	119.9	C20-C19-C18	119.9(5)
C20-C19-H29	120.1	C18-C19-H29	120.1
C19-C20-C21	120.1(5)	C19-C20-H26	120.0
C21-C20-H26	120.0	C20-C21-C22	120.6(5)
C20-C21-H28	119.7	C22-C21-H28	119.7
C21-C22-C17	120.1(4)	C21-C22-H27	120.0
C17-C22-H27	120.0	C24-C23-C28	119.0(4)
C24-C23-P1	119.9(3)	C28-C23-P1	121.1(4)
C23-C24-C25	120.2(4)	C23-C24-H41	119.9
C25-C24-H41	119.9	C26-C25-C24	120.2(4)
C26-C25-H40	119.9	C24-C25-H40	119.9
C27-C26-C25	119.9(5)	C27-C26-H39	120.0
C25-C26-H39	120.0	C26-C27-C28	120.2(5)
C26-C27-H38	119.9	C28-C27-H38	119.9
C27-C28-C23	120.4(4)	C27-C28-H28A	119.8
C23-C28-H28A	119.8	C34-C29-C30	119.1(4)
C34-C29-P1	123.0(4)	C30-C29-P1	117.9(4)

C31-C30-C29	120.9(5)	C31-C30-H35	119.5
C29-C30-H35	119.5	C30-C31-C32	119.4(5)
C30-C31-H34	120.3	C32-C31-H34	120.3
C33-C32-C31	120.4(5)	C33-C32-H33	119.8
C31-C32-H33	119.8	C32-C33-C34	120.2(5)
C32-C33-H32	119.9	C34-C33-H32	119.9
C29-C34-C33	119.9(5)	C29-C34-H31	120.0
C33-C34-H31	120.0	C11-O2-C12	115.5(3)
C14-O4-C15	121.2(5)	C14-O4-C15A	111.2(4)
C17-P1-C29	105.6(2)	C17-P1-C23	106.1(2)
C29-P1-C23	104.0(2)	C17-P1-Au1	117.28(14)
C29-P1-Au1	109.39(15)	C23-P1-Au1	113.41(14)
C6-S1-Au1	103.30(15)	C15A-C16A-H16A	109.5
C15A-C16A-H16B	109.5	H16A-C16A-H16B	109.5
C15A-C16A-H16C	109.5	H16A-C16A-H16C	109.5
H16B-C16A-H16C	109.5	O4-C15A-C16A	107.0(4)
O4-C15A-H15A	110.3	C16A-C15A-H15A	110.3
O4-C15A-H15B	110.3	C16A-C15A-H15B	110.3
H15A-C15A-H15B	108.6	O4-C15-C16	105.9(4)
O4-C15-H15C	110.5	C16-C15-H15C	110.5
O4-C15-H15D	110.5	C16-C15-H15D	110.5
H15C-C15-H15D	108.7	C15-C16-H16D	109.5
C15-C16-H16E	109.5	H16D-C16-H16E	109.5
C15-C16-H16F	109.5	H16D-C16-H16F	109.5
H16E-C16-H16F	109.5		

Table A1.14. Torsion angles (°) for I.2c.

C10-C1-C2-C3	1.9(5)	C10-C1-C2-C14	-177.9(4)
C1-C2-C3-C4	175.2(4)	C14-C2-C3-C4	-5.0(7)
C1-C2-C3-C9	-2.6(5)	C14-C2-C3-C9	177.2(4)
C2-C3-C4-C5	-175.3(5)	C9-C3-C4-C5	2.0(8)
C3-C4-C5-C6	-6.1(8)	C4-C5-C6-C7	-2.3(8)
C4-C5-C6-S1	179.0(4)	C5-C6-C7-C8	9.8(8)
S1-C6-C7-C8	-171.6(4)	C6-C7-C8-C9	-3.4(9)
C7-C8-C9-C10	176.1(5)	C7-C8-C9-C3	-8.3(8)
C4-C3-C9-C8	8.2(7)	C2-C3-C9-C8	-174.1(4)
C4-C3-C9-C10	-175.4(4)	C2-C3-C9-C10	2.3(5)
C2-C1-C10-C9	-0.5(5)	C2-C1-C10-C11	-176.1(4)
C8-C9-C10-C1	175.2(4)	C3-C9-C10-C1	-1.2(5)

C8-C9-C10-C11	-9.2(7)	C3-C9-C10-C11	174.4(4)
C1-C10-C11-O1	170.8(4)	C9-C10-C11-O1	-4.1(7)
C1-C10-C11-O2	-8.3(6)	C9-C10-C11-O2	176.9(4)
C1-C2-C14-O3	-178.4(5)	C3-C2-C14-O3	1.9(8)
C1-C2-C14-O4	3.3(6)	C3-C2-C14-O4	-176.5(4)
C22-C17-C18-C19	0.2(7)	P1-C17-C18-C19	179.9(4)
C17-C18-C19-C20	-0.8(7)	C18-C19-C20-C21	1.4(8)
C19-C20-C21-C22	-1.3(8)	C20-C21-C22-C17	0.7(7)
C18-C17-C22-C21	-0.1(7)	P1-C17-C22-C21	-179.8(3)
C28-C23-C24-C25	-1.1(7)	P1-C23-C24-C25	179.6(4)
C23-C24-C25-C26	0.0(7)	C24-C25-C26-C27	1.0(8)
C25-C26-C27-C28	-0.8(8)	C26-C27-C28-C23	-0.3(8)
C24-C23-C28-C27	1.2(7)	P1-C23-C28-C27	-179.5(4)
C34-C29-C30-C31	-0.3(7)	P1-C29-C30-C31	179.3(4)
C29-C30-C31-C32	-0.3(7)	C30-C31-C32-C33	0.5(8)
C31-C32-C33-C34	-0.1(8)	C30-C29-C34-C33	0.7(7)
P1-C29-C34-C33	-178.8(4)	C32-C33-C34-C29	-0.6(7)
O1-C11-O2-C12	-1.8(6)	C10-C11-O2-C12	177.3(4)
C13-C12-O2-C11	178.2(4)	O3-C14-O4-C15	15.1(7)
C2-C14-O4-C15	-166.4(5)	O3-C14-O4-C15A	-4.8(8)
C2-C14-O4-C15A	173.6(6)	C22-C17-P1-C29	-86.2(4)
C18-C17-P1-C29	94.1(4)	C22-C17-P1-C23	163.8(3)
C18-C17-P1-C23	-15.9(4)	C22-C17-P1-Au1	35.9(4)
C18-C17-P1-Au1	-143.7(3)	C34-C29-P1-C17	-4.4(4)
C30-C29-P1-C17	176.1(4)	C34-C29-P1-C23	107.1(4)
C30-C29-P1-C23	-72.5(4)	C34-C29-P1-Au1	-131.5(4)
C30-C29-P1-Au1	49.0(4)	C24-C23-P1-C17	-99.4(4)
C28-C23-P1-C17	81.3(4)	C24-C23-P1-C29	149.4(4)
C28-C23-P1-C29	-29.8(4)	C24-C23-P1-Au1	30.7(4)
C28-C23-P1-Au1	-148.6(3)	C7-C6-S1-Au1	25.3(4)
C5-C6-S1-Au1	-155.9(3)	C14-O4-C15A-C16A	-160.8(8)
C15-O4-C15A-C16A	75.9(17)	C14-O4-C15-C16	-90.6(10)
C15A-O4-C15-C16	-25.0(13)		

Table A1.15. Anisotropic atomic displacement parameters (Å^2) for I.2c.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au1	0.01766(9)	0.02179(9)	0.01546(8)	-0.00402(6)	0.00165(6)	-0.00968(7)
C1	0.019(2)	0.014(2)	0.020(2)	-0.0036(17)	-0.0052(18)	-0.0059(17)
C2	0.018(2)	0.014(2)	0.016(2)	-0.0004(17)	-0.0060(17)	-0.0066(17)
C3	0.016(2)	0.015(2)	0.014(2)	-0.0002(16)	-0.0031(16)	-0.0067(17)
C4	0.017(2)	0.024(2)	0.016(2)	-0.0048(18)	-0.0019(17)	-0.0069(19)
C5	0.020(2)	0.027(3)	0.013(2)	-0.0026(18)	0.0026(17)	-0.010(2)
C6	0.021(2)	0.017(2)	0.015(2)	0.0019(17)	-0.0027(17)	-0.0120(18)
C7	0.020(2)	0.021(2)	0.022(2)	-0.0090(19)	-0.0025(19)	-0.0052(19)
C8	0.016(2)	0.021(2)	0.020(2)	-0.0062(18)	0.0008(17)	-0.0083(18)
C9	0.017(2)	0.017(2)	0.018(2)	0.0005(17)	-0.0042(17)	-0.0081(18)
C10	0.015(2)	0.018(2)	0.016(2)	0.0000(17)	-0.0019(17)	-0.0073(17)
C11	0.013(2)	0.013(2)	0.021(2)	-0.0027(17)	-0.0029(17)	-0.0046(16)
C12	0.020(2)	0.028(2)	0.027(2)	-0.0099(19)	0.0057(18)	-0.0133(19)
C13	0.021(2)	0.027(3)	0.028(3)	-0.003(2)	0.001(2)	-0.012(2)
C14	0.019(2)	0.019(2)	0.022(2)	-0.0058(19)	-0.0048(19)	-0.0036(18)
C17	0.013(2)	0.015(2)	0.018(2)	-0.0057(17)	0.0028(17)	-0.0016(17)
C18	0.030(3)	0.024(3)	0.019(2)	-0.003(2)	0.002(2)	-0.007(2)
C19	0.036(3)	0.034(3)	0.018(2)	-0.005(2)	-0.002(2)	-0.010(2)
C20	0.029(2)	0.025(2)	0.032(3)	-0.016(2)	0.000(2)	-0.007(2)
C21	0.027(3)	0.020(2)	0.032(3)	-0.001(2)	-0.007(2)	-0.006(2)
C22	0.018(2)	0.025(3)	0.018(2)	-0.0013(19)	-0.0032(18)	-0.0055(19)
C23	0.021(2)	0.017(2)	0.016(2)	-0.0048(17)	-0.0002(18)	-0.0055(18)
C24	0.012(2)	0.027(3)	0.022(2)	-0.003(2)	0.0036(18)	-0.0068(19)
C25	0.021(2)	0.025(3)	0.029(3)	-0.001(2)	0.000(2)	-0.001(2)
C26	0.033(3)	0.020(2)	0.025(3)	-0.001(2)	-0.007(2)	-0.002(2)
C27	0.038(3)	0.020(3)	0.025(3)	0.002(2)	0.007(2)	-0.005(2)
C28	0.021(2)	0.024(3)	0.028(3)	-0.005(2)	0.005(2)	-0.002(2)
C29	0.014(2)	0.025(2)	0.016(2)	0.0014(18)	-0.0010(17)	-0.0083(19)
C30	0.022(2)	0.031(3)	0.020(2)	-0.005(2)	0.0055(19)	-0.012(2)
C31	0.029(3)	0.042(3)	0.026(3)	0.001(2)	-0.007(2)	-0.021(2)
C32	0.015(2)	0.047(3)	0.031(3)	0.008(2)	-0.006(2)	-0.011(2)
C33	0.018(2)	0.035(3)	0.028(3)	0.002(2)	0.000(2)	-0.001(2)
C34	0.019(2)	0.024(3)	0.023(2)	0.000(2)	-0.0028(19)	-0.0039(19)
O1	0.0235(17)	0.0312(19)	0.0216(17)	-0.0108(15)	0.0042(14)	-0.0140(15)
O2	0.0178(16)	0.0272(18)	0.0207(16)	-0.0080(14)	0.0053(13)	-0.0120(14)
O3	0.0264(18)	0.033(2)	0.0193(17)	-0.0102(15)	0.0034(14)	-0.0094(15)
O4	0.0228(18)	0.039(2)	0.046(2)	-0.0312(18)	0.0001(16)	-0.0086(16)
P1	0.0145(5)	0.0184(6)	0.0162(6)	-0.0038(5)	0.0021(4)	-0.0060(5)
S1	0.0234(6)	0.0324(7)	0.0176(6)	-0.0070(5)	0.0035(5)	-0.0193(5)
C16A	0.052(7)	0.050(7)	0.044(7)	-0.029(6)	-0.009(6)	-0.018(6)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15A	0.029(2)	0.025(2)	0.032(3)	-0.016(2)	0.000(2)	-0.007(2)
C15	0.020(2)	0.028(2)	0.027(2)	-0.0099(19)	0.0057(18)	-0.0133(19)
C16	0.047(9)	0.043(8)	0.048(9)	-0.032(7)	-0.010(7)	0.005(7)

Table A1.16. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for I.2c.

	x/a	y/b	z/c	U(eq)
H47	0.3250	0.0470	-0.0828	0.02
H52	0.8075	0.1610	-0.2067	0.022
H53	0.9330	0.2615	-0.1573	0.024
H43	0.5982	0.4184	0.0378	0.024
H42	0.4071	0.3341	0.0574	0.022
H7	0.0295	0.0999	0.2104	0.036
H8	-0.0692	0.2128	0.1497	0.036
H44	-0.1458	0.0912	0.0515	0.038
H45	-0.2093	0.0634	0.1661	0.038
H46	-0.0530	-0.0180	0.1165	0.038
H30	0.7631	0.5043	0.4637	0.031
H29	0.7957	0.6564	0.5218	0.035
H26	0.8029	0.8226	0.4156	0.033
H28	0.7660	0.8407	0.2536	0.031
H27	0.7330	0.6904	0.1943	0.024
H41	1.0012	0.2889	0.2866	0.026
H40	1.0823	0.1291	0.3994	0.033
H39	0.9101	0.0876	0.5426	0.032
H38	0.6545	0.2028	0.5711	0.037
H28A	0.5718	0.3620	0.4589	0.032
H35	0.5234	0.3563	0.2157	0.029
H34	0.2511	0.3732	0.2271	0.036
H33	0.0675	0.5136	0.3049	0.038
H32	0.1551	0.6374	0.3685	0.036
H31	0.4294	0.6223	0.3553	0.027
H16A	0.3798	-0.1559	-0.2905	0.066
H16B	0.4623	-0.1511	-0.4028	0.066
H16C	0.3444	-0.0412	-0.3652	0.066
H15A	0.6505	-0.1479	-0.3091	0.033
H15B	0.6063	-0.0284	-0.3773	0.033
H15C	0.5024	-0.1733	-0.2697	0.029

	x/a	y/b	z/c	U(eq)
H15D	0.6759	-0.1475	-0.2963	0.029
H16D	0.4095	-0.0295	-0.3947	0.068
H16E	0.5652	-0.1139	-0.4414	0.068
H16F	0.5779	0.0023	-0.4191	0.068

Table A1.17. Hydrogen bond distances (Å) and angles (°) for I.2c.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C15-H15D···O1	0.99	2.64	3.251(10)	120.5
C24-H41···O1	0.95	2.62	3.493(5)	152.9
C12-H7···O3	1.10	2.54	3.417(6)	136.4

Table A1.18. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-phenyl.

Atom	x	y	z
C	-1.11333495880069	0.38888679161954	0.00003746159882
C	-1.12025928622017	-1.00195714328472	0.00000831437156
C	0.07409697645818	-1.71605215079592	-0.00001483322163
C	1.28186957507337	-1.02381265171697	-0.00001550926570
C	1.29940003536494	0.36580334217608	0.00001112631880
C	0.09926609158030	1.08039302949739	0.00004510826834
H	-2.05157762269844	0.93091062868162	0.00006969778096
H	-2.06764599214435	-1.52810650375929	0.00001320148785
H	0.06382913717879	-2.79896661618338	-0.00003231961693
H	2.21947147633087	-1.56675807526800	-0.00003920067898
H	2.24510301263913	0.89500389812570	0.00000678754015
S	0.19850182674453	2.87007845226263	0.00014625882009
H	-1.13072027150646	3.10557699864534	-0.00023609340333

Table A1.19. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-phenyl anion.

C	-1.20996472708280	0.60927492839481	0.00645447878413
C	-1.18305177370694	-0.77721698375806	0.06638476431982
C	0.02722437748131	-1.47704721549816	0.06422639479577
C	1.21112762002493	-0.73582617696492	0.00000206391064
C	1.18722782766718	0.65085160944499	-0.06024334749300
C	-0.02558703542543	1.38857168096843	-0.06208806731106
H	-2.15856446141266	1.13478364907150	0.01098435418282
H	-2.12117658087167	-1.32470876051988	0.11977896490205
H	0.04748325282052	-2.56074590848268	0.11192074391427
H	2.16890786864275	-1.25123241971678	-0.00162588919978
H	2.11582472355634	1.20870071523848	-0.11112068749873
S	-0.05945109169353	3.13459488182226	-0.14467377330692

Table A1.20. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-4-nitro-phenyl.

Atom	x	y	z
C	-1.12684302900108	0.90842632409590	-0.00003384910643
C	-1.13701254237033	-0.47719636503497	-0.00002509704562
C	0.07080762765411	-1.16433309053701	-0.00000872204747
C	1.28764390452954	-0.49172550182335	-0.00001250945793
C	1.29294462639675	0.89265867173177	-0.00002269129861
C	0.08710584571928	1.60466975918124	-0.00002005866002
H	-2.06658416138211	1.44619344258602	-0.00002587135759
H	-2.06594549320957	-1.02954505275059	-0.00002223972854
H	2.20986015875979	-1.05486673169676	-0.00000768523186
H	2.23648720973929	1.42426049269528	-0.00002015697870
N	0.06132704137410	-2.63884206471702	0.00002076131689
S	0.18232721344169	3.38290605825195	0.00005813606555
O	1.14203557260506	-3.21752681869380	0.00002742736983
O	-1.02682172684343	-3.20352497887025	0.00004245740735
H	-1.14733224741309	3.61744585558159	0.00005009875315

Table A1.21. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-4-nitro-phenyl anion.

Atom	x	y	z
C	-1.20774846367217	1.15203599997125	0.00000541817298
C	-1.21527778479068	-0.22200108408905	0.00000593816464
C	-0.00169806633269	-0.93394130689564	0.00000228599176
C	1.21420074200504	-0.22605942810418	0.00000467145192
C	1.21128176340661	1.14795410279298	0.00000647380402
C	0.00306496592172	1.91029289211911	-0.00000411265945
H	-2.14236980767117	1.69952062481192	0.00000946989939
H	-2.14403503887548	-0.77610959621117	0.00001008686345
H	2.14103160706907	-0.78336914281220	0.00000757119056
H	2.14773947374878	1.69227012281207	0.00001263878373
N	-0.00386578259118	-2.35939471807491	-0.00000723531038
S	0.00621718563730	3.63017740020402	-0.00003033528433
O	1.08516176109621	-2.96735318556963	-0.00001196125744
O	-1.09470255495136	-2.96402268095456	-0.00001090981085

Table A1.22. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-2-methyl-phenyl.

Atom	x	y	z

C	0.52375156291846	0.35029591892585	-0.04350930147989
C	1.01663211732439	-0.93449689510560	0.20004417431850
C	0.17033063468947	-2.00555423509212	0.46063873279500
C	-1.20572971514385	-1.81101679172038	0.47481008523912
C	-1.72337944967257	-0.54694779628332	0.21809272044982
C	-0.87047087893096	0.52671709310246	-0.03908228855485
S	-1.64321426471865	2.13842316755546	-0.26553766722312
H	0.58744180160968	-2.98594754754335	0.65684586221783
H	-1.87589386485185	-2.63731818424049	0.67781730715944
H	-2.79492384285941	-0.38891479159794	0.20533185098057
H	-0.91899930564601	2.54258010314000	-1.33273836881383
H	2.09011232982574	-1.08978371989308	0.19444735539493
C	1.47506195203200	1.48620066304261	-0.29905022659307
H	2.49927955157732	1.18655144477365	-0.07563070640741
H	1.44572159399253	1.81231750005793	-1.34467762637539
H	1.22427977785371	2.35689407087833	0.31019809689235

Table A1.23. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-2-methyl-phenyl anion.

Atom	x	y	z
C	0.45975411954189	0.50441705571426	-0.14023414440825
C	0.95011740451452	-0.75990031957079	0.18431553014543
C	0.10840274975373	-1.83454582543760	0.47029293196265
C	-1.27034175776610	-1.62124103988022	0.43141788044024
C	-1.77916295441242	-0.37162241500366	0.10956415248179
C	-0.94900332453070	0.73511174105091	-0.19559425478347
H	0.52018662595444	-2.80501154500871	0.72740940671161
H	-1.95395355338739	-2.43458835891756	0.66138847332723
H	-2.85135922210757	-0.20969550288867	0.08492498871968
H	2.02826701476168	-0.90606449081586	0.21471848049569
C	1.41709689075507	1.62610635067783	-0.42545593466855
H	2.45124449409734	1.30829296701871	-0.25414169202490
H	1.31291104084220	1.98215189545246	-1.45628338319448
H	1.19146960970827	2.49491552216892	0.19885438825207
S	-1.63562913772498	2.29267396543999	-0.61017682345677

Table A1.24. Cartesian coordinates (Å) for the optimized structure of the 1-mercapto-2-methoxy-phenyl.

Atom	x	y	z
H	0.77649843657374	-3.35557663575099	0.91077492128301
H	-1.69476293444060	-3.10870376409538	0.79521387552511

C	-0.79246923796566	0.06493649348526	-0.01325911854520
S	-1.56682722038676	1.62203174886802	-0.42398244493190
C	1.15812591459195	-1.31623792180249	0.37623743197161
C	0.33103745380474	-2.40423739204419	0.64716082181583
C	-1.04816144962401	-2.26605234470277	0.58555309206261
C	-1.60308987345095	-1.03253635175865	0.25787033168855
C	0.60547723243663	-0.08140675396450	0.04366256210534
H	-2.67999790262546	-0.91820041942375	0.21096531627520
H	-0.41998601661340	2.30852217170633	-0.59815057418142
H	2.23146534240318	-1.43694833360802	0.43151168265449
C	2.75964575371357	0.93816887699115	-0.25956990837240
H	3.12112742715616	1.92330446452997	-0.54691643483326
H	3.15919103699750	0.67686518734826	0.72513073797603
H	3.09716811510908	0.20276694600493	-0.99495772271644
O	1.34255792232031	1.03530402821682	-0.23824456977718

Table A1.25. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-2-methoxy-phenyl anion.

Atom	x	y	z
H	0.48023497345443	-3.40265591818244	0.93249840220583
H	-1.98055314127765	-2.97231249966792	0.75334080525937
C	-0.87052535457763	0.18571535130219	-0.03974048754632
C	0.99012895648075	-1.37631450262563	0.39816481492042
C	0.09908905303069	-2.42597912666697	0.65414188849530
C	-1.26531106796975	-2.17733061140891	0.56101949234507
C	-1.72524463415923	-0.90920246462290	0.22152705223010
C	0.52632007908436	-0.11032987556462	0.05329571058385
H	-2.79044303753089	-0.71892585794491	0.15141453470212
H	2.05465062207464	-1.56579168513823	0.47387606637928
C	2.76329830802497	0.69882661882678	-0.19655042055559
H	3.23703442650474	1.64403217098665	-0.46743204032986
H	3.13240392398237	0.38746607285784	0.79170208474888
H	3.06044713805747	-0.06591380015407	-0.92714224730165
O	1.38231528007580	0.93902110016875	-0.20693022286842
S	-1.49684552525507	1.76369502783439	-0.44218543326839

Table A1.26. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-3-trifluoromethyl -phenyl.

Atom	x	y	z
C	-1.31105980574851	-1.97080939688873	0.51945471934337
H	1.42971149126790	-1.95459122779686	0.49648718043785
H	1.92163247660019	2.16930707621876	-0.56265288916696

H	2.89578615715549	-0.02032418108469	-0.01619748503028
S	-0.90049898677954	3.05644177145993	-0.75592201954701
C	1.27039567400322	1.33169928614327	-0.34455582632915
H	0.22877399350601	3.73120407122955	-1.05615034634177
H	-2.01995824616355	0.52451135356430	-0.10094500650084
C	1.00061021709885	-0.99366653759860	0.24948592074580
C	-0.37958022652640	-0.82422946561330	0.22295762952660
C	-0.94248627872909	0.41130819424146	-0.08672102479377
C	1.81900530485636	0.09447111236665	-0.03634031825744
C	-0.11691018172659	1.49551886277337	-0.37424365874693
F	-2.18446760134471	-1.66072536179936	1.50703615129761
F	-2.06142585392333	-2.30306012189346	-0.55794698160617
F	-0.65052813354629	-3.08605543532228	0.89625395496909

Table A1.27. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-3-trifluoromethyl-phenyl anion.

Atom	x	y	z
C	-1.28948857217507	-1.71264659962373	0.45244190916583
H	1.44831875191617	-1.71937325707022	0.44839943297432
H	1.92024878200693	2.41006595018385	-0.65975411550398
H	2.90747191522783	0.22690432334624	-0.09053420116029
C	1.27674922426009	1.57048496312517	-0.42311607784657
H	-2.00181883991524	0.78432610870561	-0.15826265310848
C	1.01992083824067	-0.76025722842821	0.19246756503011
C	-0.36524982869438	-0.57191842183586	0.16433657924603
C	-0.92515120841005	0.66264385488767	-0.14856581656297
C	1.82703398465150	0.33926512919735	-0.10629967404347
C	-0.12698717885172	1.79103991480128	-0.45995979170298
S	-0.81568108177664	3.33731455769280	-0.86267713373991
F	-2.04110400445338	-2.07737031642356	-0.62718690160382
F	-2.19205952852927	-1.43513981460491	1.43548786892600
F	-0.64020325349745	-2.84533916395348	0.84322300993018

Table A1.28. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-3-methyl-phenyl.

Atom	x	y	z
H	2.79287121731633	1.29242063492567	0.00000303678139
H	2.76807438254687	-1.17490200049042	0.00002429386426
H	-1.50209991705327	1.30511815838783	-0.00003616122183
C	0.64471670546186	1.46105048602879	-0.00002570046760
H	-0.60883148864550	3.47229916071658	0.00012389792094
C	1.84957191902378	0.75957708514455	-0.00000259905591
C	1.83099553965219	-0.63071163634902	0.00000897998694

H	-2.74615600758551	-0.69888951697542	0.00001717626998
H	-1.98169250383898	-2.02569162951986	-0.87961592749362
H	-1.98167924776734	-2.02572478094877	0.87959087092031
S	0.72306780131934	3.25207284026973	-0.00009727987147
C	0.62741935884102	-1.32464847004363	0.00000950676838
C	-0.58713295388703	-0.63248573795924	-0.00000041611645
C	-0.56382323562933	0.76145825998263	-0.00001738108690
C	-1.89564870251008	-1.38205518687935	-0.00000074276152
H	0.62734713275563	-2.40888766629008	0.00001844556310

Table A1.29. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-3-methyl-phenyl anion.

Atom	x	y	z
S	0.66417351811662	3.47980694983527	0.00001190002832
H	2.77391468001169	1.47644364598686	0.00010441357415
H	2.72226152183104	-0.98922741719038	0.00007204131104
H	-1.50115288203792	1.56027330114426	-0.00011361073167
C	0.63856856509297	1.73190481626784	-0.00001422361430
C	1.82377522571878	0.95437707434538	0.00003771364924
C	1.78784182755336	-0.43284092288776	0.00002501299302
H	-2.77955124849454	-0.40583765254354	0.00030387573054
H	-2.05983621731401	-1.75934010400515	-0.88061759426959
H	-2.05951528716504	-1.76020014076322	0.87963339903118
C	0.57616276346838	-1.12662988987864	-0.00004185321885
C	-0.62054780586133	-0.39469057982298	-0.00008661054445
C	-0.57479513957281	0.99459339868461	-0.00007960172242
C	-1.94941055382036	-1.11611859979520	-0.00019429707811
H	0.55711103247317	-2.21251387937734	-0.00004056513810

Table A1.30. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-4-methyl-phenyl.

Atom	x	y	z
C	-1.12453394815575	1.09813206889425	-0.00002831065122
C	-1.12615295193917	-0.29362974927751	-0.00001816312832
C	0.06105164002384	-1.02462516488935	-0.00000565079596
C	1.26228649967028	-0.30929948756640	0.00000284893763
C	1.27994824424631	1.07790427253714	-0.00000878806538
C	0.08151743029481	1.79554596245077	-0.00002205188895
H	-2.06708661109664	1.63282036753329	-0.00003253065076
H	-2.07604762427932	-0.81727477362061	-0.00002428030370
H	2.20502245203923	-0.84619817928026	0.00001188064562
H	2.22771302805354	1.60360674275693	-0.00000562555981
C	0.05955265815563	-2.53172470816762	0.00000957853012

H	-0.95623578893500	-2.92855842927080	0.00003755193354
H	0.57250608802621	-2.93072400226232	-0.87941704375687
H	0.57254472717730	-2.93069771509557	0.87942427876901
S	0.17926300409279	3.58604285011580	-0.00001846516075
H	-1.15034884737407	3.81867994514227	0.00009477114578

Table A1.31. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-4-methyl-phenyl anion.

Atom	x	y	z
C	-1.18744619776071	1.35261042845120	0.00000709280914
C	-1.19262672316095	-0.03728335407445	0.00002381918313
C	-0.00829652693356	-0.78120991005371	0.00001350539640
C	1.18982390934201	-0.05359638893294	0.00003257727939
C	1.20327578824295	1.33295390184315	0.00001646386830
C	0.01247019174202	2.10508226016216	-0.00001243150883
H	-2.12571186007721	1.89623920664103	0.00001537531873
H	-2.14679830129149	-0.56146576912094	0.00002338236789
H	2.13770664532805	-0.58964630130509	0.00004108628089
H	2.14869202712806	1.86410771361800	0.00003220458938
C	-0.01324410523108	-2.28937789248784	-0.00001748219918
H	-1.03515598173645	-2.67820114153005	0.00000204419903
H	0.49262598225068	-2.70749626279460	-0.87942247216067
H	0.49267966261832	-2.70753846075566	0.87933551100291
S	0.03200548953937	3.85482197033975	-0.00009067642653

Table A1.32. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-4-methoxy-phenyl.

Atom	x	y	z
C	0.20077706244662	-2.92914649041604	0.70619492343606
H	-0.48557706158629	3.82332637205885	-1.87943848605629
H	-2.37045073441313	1.11104353451994	-0.25317396449373
H	1.67291943514363	2.51813735801125	-0.42144049067541
S	-1.04446840370957	3.63086216001019	-0.66314546812372
C	-0.40919886015863	1.96931638757062	-0.37764294125446
O	1.06742219125155	-1.82713400706501	0.47631393766551
C	-0.85324378836036	-0.35953704844122	0.11632074075682
C	0.51604195265062	-0.61124597105170	0.19502637638124
C	1.42183399097906	0.43420536012450	-0.01914079020831
H	0.85132817053005	-3.77829947244323	0.90322818260455
H	-0.44427108174666	-2.75863999817163	1.57412360432389
H	-0.42125983656978	-3.14079765099632	-0.16969795268071
H	2.48255652384502	0.22741451052331	0.04877163057541

H	-1.57691484000013	-1.14472537670820	0.28366734267600
C	-1.30592799786404	0.92748020664954	-0.17620163679655
C	0.96243327756206	1.71174012582514	-0.28776500813031

Table A1.33. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-4-methoxy-phenyl anion.

Atom	x	y	z
C	-0.10524094125346	-2.47027707799874	0.69116256833720
H	-2.52342925161400	1.60969648807855	-0.46414955146253
H	1.55442722942310	2.85575591733581	-0.70722905007504
C	-0.55300394599783	2.44400395356236	-0.62421619535128
O	0.81128651902241	-1.48393000074472	0.28662860641034
C	-1.05808447526521	0.08800924865590	-0.09782106572965
C	0.29752158241391	-0.21907343557401	-0.00908219306473
C	1.23152985469991	0.79297008627974	-0.23311679875462
H	0.48549120039694	-3.34463595523430	0.96999306963677
H	-0.69994109045076	-2.14807009810184	1.55656438650370
H	-0.79822887026975	-2.75068474080059	-0.11391457101470
H	2.28791765056969	0.55214505134042	-0.16448886777475
H	-1.81581609874108	-0.66863088140091	0.07128842639982
C	-1.46377049972777	1.38881644272328	-0.40068200324795
C	0.81634345719769	2.08082201699183	-0.53415053282279
S	-1.06500232040378	4.08308298488722	-0.98178622798979

Table A1.34. Cartesian coordinates (Å) for the optimized structure of 1-mercapto-4-amino-phenyl.

Atom	x	y	z
C	-1.11495352238809	0.88939270375269	-0.00015465872710
C	-1.12576488520055	-0.49885292568287	-0.00006099458640
C	0.07012546554608	-1.23039061721057	0.00001394297475
C	1.27570748554919	-0.51382662164538	0.00002011709823
C	1.28176376480726	0.87302676568849	-0.00005008970577
C	0.08764971970833	1.59446283653628	-0.00016540971458
H	-2.06004202337341	1.41988128620218	-0.00025008663806
H	-2.07576619932222	-1.02246061054892	-0.00006152031766
H	2.21886447796126	-1.04938966732433	0.00009468678190
H	2.23126042739373	1.39585965945763	-0.00003443549880
S	0.18126608495387	3.38992875670546	-0.00041925058633
H	-1.14871953263209	3.61928791008742	0.00082821781876
N	0.06188480762439	-2.61041375138551	0.00007378807383
H	0.91770142405231	-3.13272692911955	0.00010746619826
H	-0.79997749468004	-3.12277879551303	0.00005822682898

Table A1.35. Cartesian coordinates (Å) for the optimized structure of the 1-thiolate-4-amino-phenyl anion.

Atom	x	y	z
C	-1.18240729265898	1.15074817217640	0.00001886230362
C	-1.19625701849008	-0.24096655609907	0.00001916995446
C	-0.00674513378856	-0.97660684542470	0.00000921886548
C	1.19268867443224	-0.25743319710345	0.00001906139451
C	1.19793511781789	1.13423707231539	0.00002040733808
C	0.01306906391891	1.90573766463242	-0.00000630814257
H	-2.12242232962388	1.69142818047220	0.00002446233762
H	-2.14992407765966	-0.76621879077521	0.00002477114960
H	2.13891557439185	-0.79597706862555	0.00002535745267
H	2.14531135330679	1.66187646833582	0.00002522818108
N	-0.01608205401816	-2.38313741460755	-0.00000740606052
H	0.84052499390360	-2.90126917926443	-0.00004522585308
H	-0.87952976223241	-2.88988572756977	-0.00003998671933
S	0.02592289070046	3.66646722153750	-0.00008761220161

Table A1.36. Cartesian coordinates (Å) for the optimized structure of 2-mercapto-azulene.

Atom	x	y	z
H	0.63548171245099	-2.69866289848870	0.00000192866180
H	-1.65184122582673	-3.14933061290501	-0.00000175079262
H	-3.43634368500938	-1.66430321502827	0.00000128637478
H	-3.41793154605144	0.66570035527721	-0.00000082186273
C	1.05228839841882	1.68659491492522	0.00000146510579
C	2.26740900812728	0.98135930006164	-0.00000116125843
C	0.63436802473830	-0.59961788342849	0.00000208807681
C	-0.01664694641930	-1.82926082164076	0.00000058517429
C	2.01882187480685	-0.40280689301834	0.00000047660322
C	-1.35278992853375	1.05582707403473	-0.00000093972454
C	0.00493164990899	0.75661405651255	0.00000167109830
H	-1.59445561955991	2.11557601648066	-0.00000261872306
H	2.76593917910149	-1.18290147348040	0.00000149937495
H	0.93962065407816	2.76124945394267	0.00000115269462
C	-1.38191836298662	-2.09839423539555	-0.00000055595065
C	-2.45254872914329	-1.20474489280903	0.00000014946921
C	-2.44338101186967	0.18868909301594	0.00000025057963
S	3.89925193476898	1.65954641460970	-0.00001060864010
H	3.52974461900024	2.95886624733424	0.00000590373874

Table A1.37. Cartesian coordinates (Å) for the optimized structure of the 2-thiolate-azulene anion.

Atom	x	y	z
H	0.78528432573214	-2.55801537054157	-0.00002483987133
H	-1.50663562621980	-2.96735654032821	0.00001618854434
H	-3.27957545929241	-1.45704706795994	0.00003960137096
H	-3.21152787501730	0.88158051486711	0.00001616357353
C	1.28189014997804	1.82120245310779	-0.00001445525729
C	2.53235241345413	1.12094819661813	0.00000532277718
C	0.83518684289357	-0.45298611128180	-0.00002328433217
C	0.14863451525407	-1.67562468927436	-0.00001926007811
C	2.20783594028122	-0.27529759477960	-0.00001049625411
C	-1.14258699924393	1.23767883978757	-0.00001916368685
C	0.22461711509225	0.92547208489691	-0.00002368055043
S	4.09986840244965	1.80612633176388	0.00007578487944
H	-1.37025540700355	2.30186138214802	-0.00002248339800
H	2.94844908693671	-1.06331135488441	-0.00000721374778
H	1.19754799166761	2.89979049372091	-0.00001059748740
C	-1.22115449695447	-1.91756819924604	0.00000250254793
C	-2.28745972490274	-1.01253400236545	0.00001786172430
C	-2.24347119510520	0.38508063375106	0.00000204924576

Table A1.38. Cartesian coordinates (Å) for the optimized structure of 6-mercapto-azulene.

Atom	x	y	z
H	1.08818374388685	-2.34096853254733	-0.00000115547019
C	0.46011281817613	1.10278159437818	-0.00000204960748
C	2.47856257136046	-0.04135739879330	-0.00000071330570
H	-1.16708041019601	-2.81562014107829	-0.00000422974123
C	-0.89872211268559	1.38876984472963	-0.00000100274281
C	2.72396448728665	1.33807467001019	0.00000107763755
C	1.50858287768203	2.03601464815507	0.00000029106481
H	-2.96076226469625	1.01354582386559	0.00000292963157
C	-1.99004149799577	0.52891128433164	-0.00000074303266
C	-2.00823175874233	-0.87305698486381	-0.00000261674876
C	-0.92340723352570	-1.75916198296262	-0.00000218613920
C	0.43700309620153	-1.47034009632057	-0.00000100650260
C	1.08986472954322	-0.24564606416135	-0.00000155856301
H	-1.14980023179976	2.44637959835484	0.00000307944462
H	3.22508768696674	-0.82258633136875	-0.00000066682186
H	3.70303652591230	1.79712461951995	0.00000330929519
H	1.38870518471723	3.10998493755660	0.00000157063514
S	-3.67224066138132	-1.54415536690047	-0.00002041615992
H	-3.33381755071042	-2.85069412190519	0.00002608712653

Table A1.39. Cartesian coordinates (Å) for the optimized structure of the 6-thiolate-azulene anion.

Atom	x	y	z
H	0.83653096974838	-2.50625963898666	-0.00000555330688
C	0.31032875312536	0.93266040315936	-0.00000194867683
C	2.29994761996365	-0.23561297027837	0.00000561319108
H	-1.42672612613023	-2.93591995578364	-0.00000493352826
C	-1.06343325041286	1.23912367134976	-0.00000110058600
C	2.58403184280955	1.14006092542530	-0.00000084311478
C	1.37651676315556	1.85655177976913	-0.00000297782260
H	-3.13158599394550	0.92561667855984	0.00000262720025
C	-2.17106925902883	0.42267849617092	0.00000020337281
C	-2.28161107766492	-1.00591971941372	0.00000153167471
C	-1.15087991547310	-1.88702220119338	-0.00000562230896
C	0.19931667186404	-1.62190825338025	-0.00000690276249
C	0.89980990117203	-0.40098721923805	-0.00000440528508
H	-1.28565458429223	2.30615797429489	-0.00000103712721
H	3.02396252553283	-1.04034454053691	0.00001257018992
H	3.57351621931513	1.58031036660094	0.00000365986439
H	1.26975869341454	2.93391061082279	-0.00000320621107
S	-3.86175975315340	-1.70109640734196	0.00001232523699

Table A1.40. Cartesian coordinates (Å) for the optimized structure of 2,6-dimercapto-azulene.

Atom	x	y	z
C	2.16312239754692	-0.29539783360130	0.51728935757935
C	2.12910846873076	1.10288479709545	0.59680532256779
C	1.04007186683637	1.95940235921829	0.39675630472733
C	-0.26822346581898	1.63902946811968	0.05852539622336
C	-0.85225383609439	0.39752245476256	-0.17286436321009
C	-0.18745860859984	-0.92995784890773	-0.10609009542123
C	1.14318998845754	-1.18314376399816	0.20727313901356
C	-2.18851254130266	0.16627340632225	-0.51700625521583
C	-2.37030792862711	-1.21907113846761	-0.66395892943994
C	-1.15929687517788	-1.88813497339634	-0.41558787632301
S	3.72413409571573	1.81407677549296	1.01184325726094
H	3.12442109685565	-0.75417159074643	0.72524259886721
H	1.23340359835209	3.01900912802835	0.51985548510942
H	-0.93618991574304	2.49019778342642	-0.04465984013330
H	1.43009391520417	-2.23126158034282	0.20776573388326
H	-2.94537649572524	0.92516788786864	-0.65242628404459
H	-1.00205986999619	-2.95648011279914	-0.45152982865287
H	3.34908544695521	3.11010446519164	0.98406451735124
S	-3.92594394633582	-1.94263948270768	-1.08863245805627
H	-3.50100739123331	-3.22441020055904	-1.11266518208634

Table A1.41. Cartesian coordinates (Å) for the optimized structure of the 2,6-dithiolate-azulene dianion.

Atom	x	y	z
C	2.16009063787821	-0.33528506350945	0.49915000501788
C	2.21360340578199	1.07939991061927	0.61002245991691
C	1.09049310853588	1.92205911877349	0.39596778913248
C	-0.22374521943777	1.62471311259500	0.06080570348512
C	-0.86653960305866	0.39901355707303	-0.17254133396381
C	-0.23288700881165	-0.93639794059092	-0.11192450679531
C	1.11234688292547	-1.19247982975475	0.19048327324981
C	-2.20722180144889	0.18940328354251	-0.51629804026785
C	-2.46361113532298	-1.20127107211748	-0.68046197396058
C	-1.23174217901937	-1.86867289527139	-0.42033832977803
H	3.11315971350075	-0.81754462453743	0.69607957334023
H	1.31191287917910	2.97813374941137	0.52030034005393
H	-0.87245048178314	2.49660658453620	-0.04181675514757
H	1.38222390205164	-2.25006209598824	0.17881673480642
H	-2.95363086692433	0.96255105830635	-0.65284448785350
H	-1.10121774705676	-2.94313383926089	-0.46584235287191
S	-3.98836179822804	-1.93517088022036	-1.12907229268622
S	3.75757731123856	1.82813786639370	1.04051419432201

Table A1.42. Cartesian coordinates (Å) for the optimized structure of the 2-thiolate-6- mercapto-azulene anion.

Atom	x	y	z
C	1.93738319374936	-0.42170486987795	0.54140721203990
C	1.88248237676496	0.97039914097332	0.69390999765649
C	0.77502066909924	1.81631443021511	0.53341561995750
C	-0.52223630889105	1.50708202149886	0.14792223566121
C	-1.09233478802979	0.26676543380412	-0.17548654643385
C	-0.40170851493984	-1.07130666047385	-0.16251093488654
C	0.93764179917983	-1.31388381819044	0.17174968768701
C	-2.39514697890831	0.03434828171870	-0.57000964474984
C	-2.59761897727606	-1.36254446411361	-0.82245362106528
C	-1.34432472094300	-2.00641666238728	-0.54891518338839
S	3.43389111144601	1.77293674614270	1.21138161018723
H	2.90676440751952	-0.86738004208871	0.73824104523493
H	0.96151913142382	2.86480346439054	0.73967658084447
H	-1.20198467155930	2.35390464692185	0.08431495909497
H	1.24341816374122	-2.35653983463091	0.12105846442760
H	-3.16650286379841	0.78236210320878	-0.69170475706071
H	-1.17897380780618	-3.07036132693193	-0.64904912690780
H	3.86298383533778	2.19992988031960	-0.00439973088227

S	-4.04027305610981	-2.09670847049889	-1.35654786741664

Table A1.43. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-6-thiolate-azulene anion.

Atom	x	y	z
C	2.37151897574756	-0.17952355876468	0.57634349872106
C	2.40810585726796	1.25398206925929	0.59313426912785
C	1.26197817628720	2.08500497440154	0.37058492876959
C	-0.04189181888628	1.75626509472960	0.09032930757169
C	-0.66148155642312	0.49981094571238	-0.06521602231345
C	-0.02151905153030	-0.80423945063541	0.05668007022750
C	1.33495358347488	-1.04974140596479	0.34847317277785
C	-2.01612163859797	0.27288587332128	-0.37057785176335
C	-2.21852523934242	-1.11533018807871	-0.43642228591845
C	-1.00942764131128	-1.77976380474414	-0.16836533568038
H	3.33531664097684	-0.63146492188199	0.78186437232887
H	1.48234611732890	3.14484928314424	0.43321229840653
H	-0.70974470644468	2.60723274568183	-0.03962244956902
H	1.60283141938157	-2.10455050869585	0.39839948595327
H	-2.76865871964823	1.03099123493537	-0.53737198379080
H	-0.86683075334132	-2.85078746930806	-0.13265438286651
S	-3.79699505659587	-1.90144171954625	-0.75087635083943
H	-3.60401930961066	-2.25309776534111	-2.04787772861823
S	3.91916472126725	2.01891857177546	0.90196298747541

Table A1.44. Cartesian coordinates (Å) for the optimized structure of 2-mercapto-1,3-dimethoxycarbonyl-azulene.

Atom	x	y	z
C	-0.002388	0.027560	0.066053
O	-0.112448	0.015362	1.499524
C	-0.381604	1.216805	2.078822
O	-0.521245	2.224524	1.418302
C	-0.445367	1.181021	3.542624
C	-0.484213	2.369361	4.318957
S	-0.453532	3.974379	3.624054
H	-0.333069	4.578976	4.834766
C	-0.547138	2.020779	5.699994
C	-0.537190	0.601701	5.797219
C	-0.516796	-0.142828	6.979060
H	-0.532674	0.441296	7.886480
C	-0.490270	-1.520300	7.165465
H	-0.473822	-1.842709	8.201202

C	-0.490512	-2.540476	6.222064
H	-0.485451	-3.550533	6.618147
C	-0.493861	-2.424818	4.836631
H	-0.498939	-3.359353	4.285986
C	-0.478438	-1.278995	4.049245
H	-0.460738	-1.451341	2.983305
C	-0.474949	0.067969	4.422545
C	-0.638548	2.998874	6.784833
O	-1.091734	2.487236	7.955027
C	-1.231931	3.427317	9.036524
H	-0.261454	3.828066	9.331038
H	-1.877143	4.253299	8.742447
H	-1.677657	2.863860	9.851821
O	-0.368647	4.185236	6.689078
H	0.760413	0.735531	-0.254679
H	-0.951741	0.304543	-0.393269
H	0.278007	-0.984960	-0.213417

Table A1.45. Cartesian coordinates (Å) for the optimized structure of the 2-thiolate-1,3-dimethoxycarbonyl -azulene anion.

Atom	x	y	z
C	0.19273485401870	0.06317220663628	0.12519519262168
O	0.26010781046259	0.21197901457619	1.54353208790773
C	-0.60612847261729	1.14730970733907	2.07727315184863
O	-1.32469692522802	1.80072420524477	1.35894189753561
C	-0.52292122297765	1.20206061188877	3.54251056992079
C	-0.52406483040667	2.43580384622540	4.30235867799051
S	-0.53413938399457	4.00750914672202	3.68299874145214
C	-0.51671607633338	2.03061967005730	5.69677380783935
C	-0.53693881471449	0.63065704428468	5.79328928019231
C	-0.54236475914384	-0.13815653618010	6.97064987231419
H	-0.56566041662685	0.43463556367370	7.88765201206959
C	-0.54620636783923	-1.51856021671820	7.13592006231214
H	-0.55552648177447	-1.85220754043543	8.17112580601176
C	-0.55122331829209	-2.53956398259128	6.18777193530602
H	-0.56260575646520	-3.55407749133501	6.57597050053414
C	-0.54267012974468	-2.40504183141674	4.79879740389826
H	-0.54778757741945	-3.33656768655725	4.23775765845841
C	-0.52193403124434	-1.25638384623746	4.02080665620589
H	-0.49607557869880	-1.42404749910946	2.95181722127889
C	-0.50934685491819	0.09942807531525	4.40187848507728
C	-0.45561841842254	2.98087937625361	6.81101888703625
O	-1.21416744400850	2.56783235891459	7.89230191958301
C	-1.22294071762716	3.45483011858584	9.00934596126046
H	-0.21111708677878	3.69989020230287	9.33741743032300
H	-1.73705130384881	4.38551407603898	8.75865397393902
H	-1.76439547399564	2.93154264359332	9.79718754582110

O	0.15690642987814	4.02198287952131	6.85793588134234
H	0.46390520545739	0.99219085179665	-0.37999556470362
H	-0.81050144654985	-0.22538318133318	-0.19752962432470
H	0.90714458985368	-0.72017178705652	-0.12428743105221

Table A1.46. Cartesian coordinates (Å) for the optimized structure of 6-mercapto-1,3-dimethoxycarbonyl -azulene.

Atom	x	y	z
C	-0.060152	-0.044782	-0.016870
O	-1.057815	-0.990612	0.400052
C	-1.869744	-0.596238	1.413524
O	-1.717591	0.462232	1.992921
C	-2.919425	-1.584513	1.678525
C	-3.137489	-2.752349	0.934999
H	-2.536354	-3.074498	0.100296
C	-4.257393	-3.433471	1.427650
C	-4.776125	-2.691820	2.526982
C	-5.892271	-3.031003	3.288696
H	-6.386825	-3.944863	2.981469
C	-6.459175	-2.381060	4.374924
H	-7.335258	-2.869412	4.785440
C	-6.057399	-1.198986	5.007555
S	-6.996913	-0.609050	6.411703
H	-7.893490	-1.616529	6.455703
C	-4.970670	-0.376170	4.677239
H	-4.833353	0.497508	5.306228
C	-4.038233	-0.514911	3.659828
H	-3.288545	0.266247	3.599538
C	-3.917115	-1.512850	2.691605
C	-4.787809	-4.696134	0.906070
O	-4.031318	-5.179760	-0.112121
C	-4.394396	-6.477474	-0.609631
H	-5.440966	-6.502588	-0.912875
H	-4.224879	-7.236152	0.156205
H	-3.745537	-6.654583	-1.462855
O	-5.774363	-5.278837	1.314138
H	0.533521	0.298522	0.829963
H	-0.531242	0.816220	-0.493671
H	0.562710	-0.578413	-0.730970

Table A1.47. Cartesian coordinates (Å) for the optimized structure of the 6-thiolate-1,3-dimethoxycarbonyl -azulene anion.

Atom	x	y	z

C	-0.06578776281561	-0.06692092976116	-0.02828547250429
O	-1.02829582847088	-1.02842363631606	0.39844180700351
C	-1.87214214674133	-0.61746292168249	1.41008095440831
O	-1.70360981183072	0.46376201081282	1.95047907519783
C	-2.90918116761141	-1.59445788584187	1.67854045375282
C	-3.12462311845917	-2.75950687389517	0.92944577489047
H	-2.52781559212758	-3.08005449817008	0.09159868459103
C	-4.24799742550225	-3.43394229580507	1.42706893061755
C	-4.76266715843106	-2.67697669723034	2.53831177335534
C	-5.88736030854682	-3.01855386658464	3.32565511120259
H	-6.37568803195194	-3.93790683893237	3.02483206753057
C	-6.45476901841132	-2.37702501543116	4.39668341227791
H	-7.32614328108110	-2.86125348899078	4.82263486572137
C	-6.10519441943252	-1.15891990357687	5.06645799878642
S	-7.08284030161658	-0.63542856139237	6.37468600432856
C	-4.97144350790855	-0.36490658162957	4.68892383310009
H	-4.83845990498952	0.51107433917678	5.31397429069127
C	-4.04851584392156	-0.52060499649427	3.68508388615612
H	-3.29295879275303	0.25489564597768	3.62428566575277
C	-3.92327106515990	-1.52908905359858	2.69884153515312
C	-4.78063608812452	-4.67418013469253	0.89754846951569
O	-4.01706602743965	-5.16538396449951	-0.14290656437110
C	-4.38377208487892	-6.45789382110624	-0.62065544278605
H	-5.43565924965122	-6.49662930654710	-0.90934308423980
H	-4.20392111257799	-7.21991178846415	0.14249732226528
H	-3.74867657612494	-6.64532508006408	-1.48471841015777
O	-5.77017549725977	-5.28067841782636	1.27359855396677
H	0.51900599525802	0.31559694961974	0.80993857836714
H	-0.55163208783146	0.77764828634595	-0.52433162178867
H	0.57918721639332	-0.59132067340018	-0.73279845278483

Table A1.48. Cartesian coordinates (Å) for the optimized structure of 2,6-dimercapto-1,3-dimethoxycarbonyl -azulene.

Atom	x	y	z
C	-0.35906879383691	0.00775326957265	-0.00740549738676
O	-0.37090609803585	-0.00941791795580	1.43034234475146
C	-0.16606398219678	1.19399273404343	2.03350359625531
O	0.02920913930594	2.20230891777034	1.38851317731344
C	-0.24027877875424	1.15219797477688	3.49670050169752
C	-0.25805059327659	2.33500677552243	4.28362201346862
S	-0.10913644882389	3.94291608782821	3.60637196564177
H	-0.15860017564912	4.54528316457337	4.82229195248037
C	-0.42700200412191	1.97798350144205	5.65269040622809
C	-0.44542527609867	0.55693016776011	5.73417066642544
C	-0.49182312331991	-0.20299836529335	6.90557991417496
H	-0.56039331595368	0.37144724940646	7.81801219161985

C	-0.46262130805325	-1.57642869902175	7.09702303588935
H	-0.49550428589515	-1.88366705112387	8.13690857332121
C	-0.40240691194977	-2.60475481127075	6.15411008166611
S	-0.37821175835885	-4.30818494760596	6.70238919589759
H	-0.45223869219283	-4.06152937399740	8.02727677462863
C	-0.35286993232344	-2.46363584857481	4.76266675930271
H	-0.32139545503337	-3.38898975752956	4.19622437701800
C	-0.31935063340770	-1.31295620232297	3.99330719944217
H	-0.26710349190035	-1.48312252701574	2.92773767696546
C	-0.33416243223201	0.03621911707976	4.36743023165124
C	-0.61959004892318	2.94591978377690	6.73414425969541
O	-1.18024036500618	2.41557686871686	7.85213597957649
C	-1.46686626983516	3.35093740083877	8.90919849411371
H	-0.55279181443744	3.82085766655913	9.27290906317006
H	-2.14651665670706	4.12602002118715	8.55614679102988
H	-1.93554252525699	2.76180449663833	9.69366471702296
O	-0.35519609359765	4.13575081299904	6.67581383469342
H	0.62768429646009	0.28094589046871	-0.38311397845058
H	-1.08989174258897	0.71933402842454	-0.38919767428005
H	-0.61963183799912	-1.00360319767319	-0.31117965502383

Table A1.49. Cartesian coordinates (Å) for the optimized structure of the 2,6-dithiolate-1,3-dimethoxycarbonyl-azulene dianion.

Atom	x	y	z
C	-0.11098601763023	-0.12650280423780	0.01815370733288
O	-0.03268077087098	0.02423160763300	1.42434207057696
C	-0.65657640416430	1.18034587487516	1.93419986717705
O	-1.09940436913599	1.98839888502663	1.14239610145878
C	-0.65646810155278	1.21887947535866	3.38435611040807
C	-0.67590985732235	2.44445553011084	4.15824029835932
S	-0.66328812987139	4.05006561115897	3.55561535337682
C	-0.70839906677722	2.03342946732051	5.54797369560664
C	-0.71733997270279	0.60601285714694	5.62449217361934
C	-0.70904994824795	-0.18922023429854	6.79188360422800
H	-0.71981369874029	0.37921500460926	7.71206265847648
C	-0.70262589532131	-1.55861110286831	6.98654592990675
H	-0.69356014521895	-1.87018112319482	8.02704330943359
C	-0.72129920186918	-2.64651434014093	6.07498693820928
S	-0.73933811489342	-4.28623819633899	6.69482451372405
C	-0.72646129203462	-2.43252390409950	4.67217267367847
H	-0.74894490411180	-3.35236120426122	4.09546060360452
C	-0.69509329850783	-1.27308734387025	3.91691544332289
H	-0.68080735946682	-1.44928786727901	2.84984375142774
C	-0.66674649972519	0.09450659957506	4.26874948893133
C	-0.73273139248104	2.95861338328897	6.66531987937995
O	-1.39177117959068	2.42677777956336	7.78952886060548
C	-1.43940005155802	3.28238470180888	8.91840436439937

H	-0.44485836352625	3.63018494819976	9.21302090008418
H	-2.05407999469167	4.16650334651436	8.72331489686879
H	-1.88664405086766	2.69201096911167	9.72082257477228
O	-0.28715818165488	4.08576882668006	6.74266461602309
H	0.35145762427656	0.71427823004387	-0.50548388688215
H	-1.14739473068750	-0.20545986244701	-0.32628803991150
H	0.42527684894654	-1.04891895498955	-0.21366900819846

Table A1.50. Cartesian coordinates (Å) for the optimized structure of the 2-thiolate-6- mercapto-1,3-dimethoxycarbonyl-azulene anion.

Atom	x	y	z
C	-0.09910885056090	-0.06058387027743	0.01688232646874
O	0.00260026503692	0.10094968887550	1.43209890669064
C	-0.82721430470499	1.06136247134711	1.97630430066436
O	-1.54620273154476	1.72670645548048	1.26937561693522
C	-0.71012423729164	1.12841507941560	3.43889250891974
C	-0.73183510676057	2.36922510897676	4.19174861296552
S	-0.78935400536891	3.93561412032300	3.57150492222519
C	-0.69203811346415	1.97506013226861	5.58959047708192
C	-0.66555918787027	0.58073628713567	5.69531474606734
C	-0.62059997289175	-0.17969963096776	6.87872807763088
H	-0.64272505215555	0.39986358770282	7.79180036456842
C	-0.57775109636113	-1.55352680947967	7.06781288156784
H	-0.55213600380943	-1.87073845832573	8.10505962759188
C	-0.57403436147325	-2.59331860292222	6.13199305009767
S	-0.47962903448706	-4.28614489554231	6.79147975716397
H	-1.80858080573923	-4.55010484108267	6.87204500478153
C	-0.57593928081193	-2.46516112791472	4.73886458912641
H	-0.54466927698835	-3.39945557805463	4.18874003654900
C	-0.60816596383961	-1.32365404430429	3.95216208593642
H	-0.58459333245161	-1.50933134872905	2.88681833533989
C	-0.64486769363538	0.03739345102867	4.30944677655318
C	-0.64464235384341	2.93413216158700	6.70005373611725
O	-1.41092904887850	2.52243019569169	7.77242751493904
C	-1.43642561964544	3.41294254040359	8.88811797540138
H	-0.42922185171554	3.65920352123422	9.22880337526455
H	-1.94852298548488	4.34162352858484	8.62708332994860
H	-1.98729807355119	2.89018730399368	9.66936723885703
O	-0.03472206392872	3.97617129168008	6.74329566844703
H	0.17569844521419	0.85903194507600	-0.50302297779367
H	-1.11375184594782	-0.33652764776585	-0.27953031720532
H	0.59713245495484	-0.85762568543898	-0.23965172890172

Table A1.51. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-6-thiolate-1,3-dimethoxycarbonyl-azulene anion.

Atom	x	y	z
C	-0.03577692754907	0.00465871013661	0.00885000401718
O	-0.11393522733027	-0.00696783277418	1.43453470166567
C	-0.35615810886656	1.21282910506044	2.02195772417380
O	-0.48197485251664	2.21001711948255	1.33200276946393
C	-0.41914467835137	1.17998217149645	3.47075358778978
C	-0.44983553124147	2.36356440406533	4.24454508632027
S	-0.42176578900701	3.99326494240909	3.55142322096618
H	-0.30019854739881	4.58885080855216	4.76407445829468
C	-0.52574651920137	2.01391514538363	5.61942723973222
C	-0.52544795520223	0.57311338129520	5.70333753269473
C	-0.51530089342978	-0.19703710443337	6.89263974595096
H	-0.53432987749613	0.38617626938745	7.80239391432363
C	-0.49031480394996	-1.55367912083159	7.09742319331912
H	-0.48056127355824	-1.86412242025098	8.13677424416504
C	-0.48422253372920	-2.65410555450471	6.18306639907370
S	-0.48316330301939	-4.25426324389232	6.80254963146789
C	-0.47636755205644	-2.45656865087267	4.76580470992477
H	-0.47643535596112	-3.38491748955546	4.20517065668891
C	-0.45669352824087	-1.31251971348041	4.00796248736078
H	-0.43436393081146	-1.48463968369735	2.94113346871444
C	-0.45681421001674	0.05751645023801	4.37235887597603
C	-0.63517223687059	2.97777541789482	6.69513985966194
O	-1.13339614587977	2.45660147150243	7.85963605678860
C	-1.25292653378488	3.37296598668065	8.94990445565687
H	-0.28251731449702	3.79014541274010	9.22759655732830
H	-1.92116477299620	4.19667990000845	8.69571036726046
H	-1.66570726392085	2.79100736816360	9.77229768014122
O	-0.35524189976819	4.17194051589950	6.64261875368380
H	0.73144713681066	0.69810406987706	-0.33778307847006
H	-0.98889189923568	0.29728698388188	-0.43769765370034
H	0.22038171907665	-1.01407855986239	-0.27900586043451

Table A1.52. Cartesian coordinates (Å) for the optimized structure of 2-mercapto-6-[thiolate-gold(I)-trimethylphsophine]-1,3-dimethoxycarbonyl-azulene.

Atom	x	y	z
C	0.01232955541810	-0.00690585022272	-0.00952409775980
C	0.21493349012890	1.43499155590521	-0.42372986832937
H	-0.75484168555229	1.90217599067400	-0.61028115965979
H	0.81007010735390	1.49964639257332	-1.33573901056158
H	0.72422194982258	1.99911926092255	0.35913134365278

O	1.31595232748345	-0.58030042870107	0.22757824006103
C	1.35174748798845	-1.87607481662202	0.61775946387645
C	2.71449784581653	-2.36419078738790	0.83649285340842
C	3.93205098165487	-1.65170412103661	0.68666127174760
C	5.02303986650640	-2.51727219125764	1.00841973277196
C	4.47493363269156	-3.79146631022938	1.36377462361437
C	5.17899757450779	-4.94188612661484	1.74682076802141
C	4.73735410565922	-6.20482842260227	2.10286697686241
C	3.43698660954042	-6.73089138053449	2.19451558709796
C	2.26334802791462	-6.01118563179235	1.91765375982496
C	2.09564131144388	-4.70055943094060	1.51288786852244
C	3.02997561009873	-3.68875856972713	1.25458617995194
H	1.06803737908272	-4.39391070669646	1.36672909494083
H	1.34098208355430	-6.56699657117345	2.03831634220904
S	3.38695566300687	-8.43648053020313	2.70510969419905
Au	1.15297074456552	-9.14105173590058	2.78837027083154
P	-1.00910922951349	-9.95322866612750	2.90920459263394
C	-2.31010761950549	-8.66003293108213	2.72954939885806
H	-2.18934132315554	-7.91128264539190	3.51269920457355
H	-2.20242535836879	-8.16480816071940	1.76420369323309
H	-3.30644527938467	-9.10058864731066	2.80004443470517
C	-1.44259901293465	-11.20190249625095	1.62353879644453
H	-0.77452226472659	-12.05875684090190	1.70939020302821
H	-2.47591733324741	-11.53504478735123	1.73781286108266
H	-1.31098381175967	-10.76330040117378	0.63428616850869
C	-1.42763851597701	-10.79066218871638	4.49848696368850
H	-0.75700251235463	-11.63635165479224	4.64925157909386
H	-1.28810353372388	-10.09184324262202	5.32324612292969
H	-2.46048714447107	-11.14378266324370	4.49189779561030
H	5.52907036227178	-6.90286035432707	2.35341378807221
H	6.25178298612567	-4.82852252146989	1.76847090418222
C	6.42577472928215	-2.11404483451786	0.96587804134955
O	7.30486137607119	-3.09177605761359	1.30753284086904
C	8.70646988316999	-2.73462358352024	1.27840768602400
C	9.49918802455042	-3.95945062774432	1.68078330679933
H	10.56612747077828	-3.72431088909122	1.66898029241291
H	9.32543707840750	-4.78640572988531	0.98969267279612
H	9.23535968193720	-4.28697648001222	2.68793856601904
H	8.96437086267776	-2.39644962077720	0.27360007139908
H	8.87296168348206	-1.89998389353198	1.96148382697160
O	6.84100121026794	-1.00498421788795	0.65577638130024
S	4.03703511539743	0.03087580918091	0.18108868519939
H	5.39437518656784	0.04804484719222	0.25464411363045
O	0.32847365410331	-2.52473833828722	0.75956595586881
H	-0.49288281685727	-0.58642337229365	-0.78515239150751
H	-0.58077721779690	-0.08901039816203	0.90336450893962

Table A1.53. Cartesian coordinates (Å) for the optimized structure of the 2-thiolate-6-[thiolate-gold(I)-trimethylphsophine]-1,3-dimethoxycarbonyl-azulene anion.

Atom	x	y	z
C	0.19356686545743	-0.05503408502423	-1.00669826947156
C	-0.10379495893931	1.22630458878987	-0.25277804889165
H	-0.80180811683230	1.84524093467202	-0.82496603922807
H	0.81498114937878	1.78924989871173	-0.08387502357758
H	-0.55052357766221	1.00952815523199	0.71966664211490
O	1.12903115170932	-0.79985376454021	-0.22055539511181
C	1.59421052190481	-1.95526040297732	-0.75996919744525
C	2.65713447842640	-2.57068372708496	0.03090795443512
C	3.64481969475615	-1.89629754546296	0.85397043613988
C	4.44228794249363	-2.94763894761447	1.44076198184873
C	4.01308502333833	-4.19578724619614	0.99252021301400
C	4.54030284231564	-5.44733642330404	1.36234257607268
C	4.14727858959286	-6.72873943728991	1.01791848809092
C	3.10347041395481	-7.15853144501921	0.18279120901867
C	2.23608950273317	-6.33706497926982	-0.54032733774767
C	2.13534589928025	-4.94839524237832	-0.58823295245553
C	2.87011917722633	-3.96154798034265	0.07989742050000
H	1.36815550936642	-4.56630953398617	-1.25038247101947
H	1.51631351527852	-6.86516161943467	-1.15625660910155
S	2.89051342435457	-8.96393294157227	-0.00031901605170
Au	1.30049296836867	-9.28256614248531	1.67302157105364
P	-0.27263368126236	-9.42378191864964	3.35176852395718
C	-0.42883685346410	-7.87070310063489	4.33857444050295
H	0.53419400277942	-7.63298673045052	4.79066511115129
H	-0.69666838747254	-7.04913144017997	3.67414840446021
H	-1.18452357327196	-7.97064048470079	5.12108596546891
C	-2.01093524801894	-9.75683620023431	2.81501074187735
H	-2.04908927926164	-10.71044749243089	2.28738958525454
H	-2.69227419331165	-9.78542271941223	3.66839439216190
H	-2.32601235974604	-8.97417102343852	2.12434084252767
C	0.01080631100968	-10.71786461473286	4.64250072685815
H	0.02333750169546	-11.70115786786871	4.17137087461198
H	0.98243065384178	-10.55195193383916	5.10838661399350
H	-0.76782010137387	-10.69206539679293	5.40878727278189
H	4.72992784661806	-7.52579454434686	1.46666783028119
H	5.39624754755351	-5.39966779556396	2.02628461382241
C	5.52220734569391	-2.71560572917437	2.41485634851120
O	6.69754960656334	-3.32255734236340	2.03358687944903
C	7.80084586473467	-3.17445963094649	2.93968340002410
C	9.00812167402744	-3.83567734821171	2.30315214193366
H	9.87707783773502	-3.74167205142118	2.96086728337178
H	9.24612750709105	-3.36493454769629	1.34781173863324
H	8.82493691224948	-4.89677126039902	2.12269918324541
H	7.97387645250413	-2.11228222327524	3.12559292158442
H	7.54970605501730	-3.63388842858397	3.90040142548844
O	5.44621430447988	-2.10069140942622	3.45203218600080
S	3.96624066747338	-0.23415960530582	0.99814577706023
O	1.10680453674068	-2.40861023201266	-1.78672768325933

H	0.62724126910414	0.14951200017797	-1.98946746203361
H	-0.71063523623152	-0.64909304150833	-1.16966121190727

Table A1.54. Cartesian coordinates (Å) for the optimized structure of 2-mercapto-1,3-dimethoxycarbonyl-2',6-biazulene.

Atom	x	y	z
C	-6.352973	-1.700799	-2.808393
C	-6.343793	-3.088847	-2.934809
C	-5.382972	-4.017363	-2.533569
C	-4.159375	-3.790166	-1.909492
C	-3.583237	-2.581805	-1.531419
C	-4.171908	-1.215339	-1.663183
C	-5.390466	-0.872169	-2.237406
C	-2.327628	-2.419746	-0.939943
C	-2.108007	-1.047824	-0.690540
C	-3.239538	-0.324256	-1.122878
H	-7.227616	-1.198735	-3.207611
H	-7.217081	-3.513781	-3.420118
H	-5.617593	-5.054484	-2.747855
H	-3.564989	-4.674852	-1.695891
H	-5.620518	0.190358	-2.238152
H	-1.661471	-3.227690	-0.674350
H	-3.350525	0.749849	-1.100927
C	-1.025022	0.703668	0.664594
C	-0.890120	-0.459035	-0.112067
C	0.327661	-1.095164	-0.391093
C	1.629588	-0.759275	-0.049841
C	2.133828	0.332036	0.662380
C	1.332280	1.406767	1.262240
C	-0.064053	1.503646	1.259041
C	3.501637	0.603616	0.957327
C	3.546640	1.800141	1.734890
C	2.228909	2.304765	1.894110
H	-2.045312	1.027734	0.836910
H	0.247565	-1.986263	-1.002830
H	2.378389	-1.441202	-0.420919
H	-0.454688	2.352011	1.802720
C	4.687447	-0.138147	0.528434
C	1.955344	3.585608	2.553871
S	4.957884	2.580686	2.410297
O	2.764346	4.209476	3.206884
O	0.697035	4.063407	2.338190
C	0.434571	5.371942	2.877865
O	5.835157	0.087693	0.881418
O	4.432227	-1.136395	-0.355916
C	5.576301	-1.879063	-0.812177
H	5.810639	1.652230	1.901695

H	-0.590559	5.599060	2.595384
H	0.547475	5.378115	3.962199
H	1.117695	6.103546	2.446940
H	5.177017	-2.632345	-1.486975
H	6.272170	-1.225038	-1.337944
H	6.092636	-2.348572	0.024907

Table A1.55. Cartesian coordinates (Å) for the optimized structure of the 2-thiolate-1,3-dimethoxycarbonyl-2',6-biazulene anion.

Atom	x	y	z
C	-0.069301	-0.099563	0.024590
O	0.378499	-1.309622	-0.591935
C	1.403126	-1.168040	-1.497626
C	1.761756	-2.454306	-2.123511
C	0.879694	-3.328552	-2.751854
C	1.690534	-4.426422	-3.339750
C	1.192192	-5.521652	-4.072501
C	-0.098179	-5.849179	-4.432989
C	-1.328752	-5.195470	-4.196754
C	-2.534486	-5.801839	-4.740981
C	-2.687918	-7.153047	-5.157563
C	-3.984822	-7.364045	-5.614987
C	-4.511577	-8.570719	-6.078440
C	-5.787903	-8.842007	-6.562263
C	-6.872246	-7.977335	-6.717958
C	-6.969129	-6.618478	-6.412779
C	-6.011448	-5.769826	-5.865474
C	-4.697147	-6.053769	-5.492359
C	-3.781120	-5.153676	-4.957574
H	-3.987627	-4.109470	-4.777210
H	-6.328424	-4.743631	-5.696185
H	-7.928154	-6.158882	-6.633775
H	-7.767733	-8.425945	-7.138804
H	-5.959153	-9.866811	-6.878344
H	-3.822123	-9.411752	-6.065192
H	-1.935966	-7.925255	-5.086772
C	-1.459170	-3.989228	-3.469816
C	-0.519769	-3.191522	-2.849591
H	-0.924430	-2.327956	-2.336303
H	-2.477577	-3.636406	-3.350896
H	-0.168769	-6.748496	-5.034313
H	1.951797	-6.202538	-4.433404
C	3.019282	-4.184920	-2.998860
C	3.119079	-2.949562	-2.247528
S	4.521165	-2.237988	-1.646024
C	4.153570	-5.083470	-3.264889
O	4.998338	-5.441255	-2.478607

O	4.160817	-5.526900	-4.566543
C	5.193318	-6.461153	-4.889645
H	4.985550	-6.794102	-5.905441
H	6.173730	-5.983360	-4.840062
H	5.184709	-7.310091	-4.203571
O	1.896043	-0.087813	-1.718176
H	-0.845604	-0.398395	0.726916
H	0.747905	0.396819	0.550187
H	-0.475984	0.591813	-0.717413

Table A1.56. Cartesian coordinates (Å) for the optimized structure of the [Sodium][2-mercapto-6-thiolate-1,3-dimethoxycarbonyl-azulene anion].

Atom	x	y	z
C	-0.075046	-0.072868	0.022154
O	-0.127620	-0.067561	1.457936
C	-0.388567	1.140828	2.032835
O	-0.571611	2.132825	1.358649
C	-0.414167	1.120756	3.496778
C	-0.541909	2.308723	4.264472
S	-0.658114	3.908103	3.550787
H	-0.658342	4.530581	4.756727
C	-0.553413	1.967137	5.647833
C	-0.413495	0.545807	5.743932
C	-0.270185	-0.204755	6.918842
H	-0.238456	0.380904	7.826547
C	-0.159873	-1.572355	7.118013
H	0.021597	-1.866032	8.150233
C	-0.197786	-2.656110	6.202022
S	-0.285048	-4.303998	6.825903
C	-0.161755	-2.483154	4.799131
H	-0.105191	-3.411415	4.242600
C	-0.204767	-1.337179	4.031874
H	-0.154796	-1.510558	2.966881
C	-0.333335	0.017915	4.390866
C	-0.723727	2.932967	6.727230
O	-0.949665	2.371342	7.950161
C	-1.085230	3.296087	9.041152
H	-0.160249	3.853386	9.195013
H	-1.891798	4.003325	8.851573
H	-1.310715	2.682996	9.911078
O	-0.696547	4.148860	6.614198
H	0.662611	0.642105	-0.339873
H	-1.047318	0.181264	-0.402344
H	0.210648	-1.085681	-0.253557
Na	-2.303261	-3.108475	7.883525

Table A1.57. Cartesian coordinates (Å) for the optimized structure of the [Sodium][2,6-dithiolate-1,3-dimethoxycarbonyl-azulene dianion].

Atom	x	y	z
C	0.292847	-0.103428	0.155648
O	0.219547	0.037593	1.573987
C	-0.462665	1.166769	2.013888
O	-0.891947	1.964051	1.213991
C	-0.551102	1.224606	3.473853
C	-0.479072	2.456648	4.235371
S	-0.257464	4.028325	3.650171
C	-0.640289	2.065298	5.620619
C	-0.824126	0.681088	5.714876
C	-1.000907	-0.070830	6.895106
H	-1.072689	0.522308	7.797758
C	-1.073328	-1.438536	7.101355
H	-1.148148	-1.744968	8.139758
C	-1.031367	-2.515885	6.191125
S	-0.733661	-4.166077	6.855588
C	-1.031745	-2.354642	4.789358
H	-1.111348	-3.287178	4.236931
C	-0.897508	-1.216695	3.995444
H	-0.876513	-1.413373	2.931083
C	-0.740711	0.136177	4.343677
C	-0.514927	2.986432	6.756761
O	-1.478847	2.757637	7.718165
C	-1.361458	3.540990	8.906537
H	-0.358290	3.465270	9.332193
H	-1.574047	4.592617	8.703204
H	-2.097171	3.138204	9.601343
O	0.322057	3.844003	6.911593
H	0.760970	0.769425	-0.302492
H	-0.699087	-0.231238	-0.284916
H	0.897633	-0.991899	-0.024269
Na	1.373122	-2.980007	5.874220

Table A1.58. Cartesian coordinates (Å) for the optimized structure of the 2-[thiolate-gold(I)-trimethylphsophine]-1,3-dimethoxycarbonyl-azulene.

Atom	x	y	z
C	0.067717	-0.025332	0.024739
O	1.153774	-0.858816	0.475382
C	2.371753	-0.589743	-0.078194
C	3.418606	-1.480538	0.457392
C	3.666230	-1.817409	1.822049

C	4.652631	-2.857426	1.854081
C	5.064306	-3.128068	0.517290
C	6.028994	-4.065846	0.129154
C	6.492685	-4.376714	-1.154199
C	6.110133	-3.849992	-2.390761
H	6.624033	-4.263539	-3.262968
C	5.154041	-2.862469	-2.660370
C	4.346907	-2.153436	-1.770196
C	4.284093	-2.236720	-0.370929
H	3.683036	-1.408612	-2.216523
H	5.022140	-2.606977	-3.715672
H	7.266176	-5.149600	-1.191140
H	6.488816	-4.610073	0.955966
C	5.198853	-3.549375	3.029380
O	4.373963	-3.452342	4.113350
C	4.876817	-4.056533	5.323504
H	5.009058	-5.139297	5.191721
H	5.840473	-3.613424	5.608967
H	4.116311	-3.848888	6.083758
O	6.254456	-4.177427	3.069268
S	3.010203	-1.000513	3.243698
Au	2.915452	1.213819	2.510233
P	2.979012	3.373232	1.731979
C	1.341753	4.203687	1.493129
H	0.805380	4.239679	2.449951
H	1.474562	5.224786	1.107754
H	0.745001	3.621618	0.779539
C	3.928611	4.581980	2.762510
H	3.457548	4.668655	3.749894
H	4.952594	4.212616	2.899970
H	3.956079	5.570172	2.281593
C	3.771783	3.459513	0.066771
H	4.824305	3.161398	0.155782
H	3.272989	2.744486	-0.601479
H	3.710431	4.476973	-0.345453
O	2.520608	0.239193	-0.973990
H	0.218449	1.011724	0.358905
H	-0.013937	-0.042525	-1.070322
H	-0.829704	-0.444010	0.490878

Table A1.59. Cartesian coordinates (Å) for the optimized structure of the 6-[thiolate-gold(I)-trimethylphsophine]-1,3-dimethoxycarbonyl-azulene.

Atom	x	y	z
C	0.186781	0.138476	-0.043399
O	1.480802	-0.455672	0.181280
C	1.452691	-1.777550	0.560555
C	2.800612	-2.305136	0.769376

C	4.000607	-1.581387	0.626706
C	5.099093	-2.415245	0.912212
C	4.594683	-3.714972	1.243939
C	5.364815	-4.838812	1.584852
C	4.966641	-6.129790	1.913132
C	3.667640	-6.687726	2.004260
C	2.452063	-6.005314	1.763972
C	2.226011	-4.684452	1.396083
C	3.135743	-3.644425	1.153749
H	1.177887	-4.398244	1.270157
H	1.552277	-6.614739	1.887184
S	3.676999	-8.408990	2.463035
Au	1.474249	-9.148821	2.647745
P	-0.642737	-10.003519	2.901731
C	-1.987538	-8.755444	2.682667
H	-1.854984	-7.945109	3.411045
H	-1.927010	-8.325575	1.674631
H	-2.975187	-9.216875	2.824283
C	-1.087908	-11.356672	1.723488
H	-0.382876	-12.189515	1.842193
H	-2.111266	-11.714117	1.905973
H	-1.008334	-10.982043	0.694786
C	-0.975476	-10.735484	4.567135
H	-0.270056	-11.555850	4.750378
H	-0.820101	-9.969136	5.337140
H	-2.004799	-11.116093	4.629146
H	5.781527	-6.822856	2.139331
H	6.443281	-4.658306	1.588857
C	6.507308	-2.017599	0.878067
O	7.473319	-2.724970	1.149051
O	6.653196	-0.704823	0.494360
C	8.018165	-0.240714	0.441532
H	8.489642	-0.299261	1.432528
H	8.608214	-0.839782	-0.265557
H	7.956006	0.800070	0.106583
H	4.069020	-0.536353	0.340039
O	0.396139	-2.391032	0.691717
H	-0.358139	-0.396388	-0.833787
H	-0.416544	0.122104	0.875167
H	0.392110	1.169854	-0.349002

Table A1.60. Full table used in the calculations of H^+ for the series of mercaptoarenes in Chapter 1, Table 1.

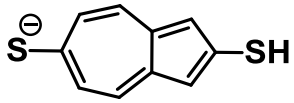
Compound	HA (g)	HA (DMSO)	A- (g)	A- (DMSO)	HA (solvation)	A- (solvation)	HA (g) in kcals	A- (g) in kcals	Exp. pKa (DMSO)	H+	Calc. pKa	Percent Error	Absolute Error
SH-phenyl	-630.25	-630.26	-629.71	-629.80	-4.51	-57.53	-397059.84	-396718.77	10.28	274.02	10.31	0.25	0.03
1-SH-4-NO_2-phenyl	-834.75	-834.76	-834.24	-834.32	-9.20	-49.46	-525890.57	-525570.08	5.50	272.73	4.58	16.82	0.92
1-SH-2-Me-phenyl	-669.53	-669.54	-668.99	-669.08	-4.28	-55.66	-421802.90	-421462.92	10.70	274.00	10.71	0.11	0.01
1-SH-2-MeO-phenyl	-744.73	-744.74	-744.18	-744.28	-5.98	-61.63	-469179.74	-468833.76	11.35	274.84	11.97	5.49	0.62
1-SH-3-CF_3-phenyl	-967.31	-967.32	-966.79	-966.87	-4.94	-51.94	-609407.09	-609075.20	8.09	273.85	7.99	1.24	0.10
1-SH-3-Me-phenyl	-669.53	-669.54	-668.99	-669.08	-4.59	-58.33	-421803.40	-421461.77	10.55	273.49	10.19	3.42	0.36
1-SH-4-Me-phenyl	-669.53	-669.54	-668.99	-669.08	-4.62	-58.13	-421803.22	-421460.89	10.82	274.07	10.88	0.53	0.06
1-SH-4-MeO-phenyl	-744.73	-744.74	-744.18	-744.28	-5.45	-59.22	-469180.15	-468836.30	11.19	274.82	11.80	5.46	0.61
1-SH-4-NH_2-phenyl	-685.59	-685.60	-685.03	-685.14	-9.01	-64.84	-431918.71	-431571.75	12.51	274.07	12.57	0.46	0.06
										Average	273.99	3.75	0.31
										Std. Dev.	0.64	5.36	0.34

Table A1.61. Full table used in the calculations of pKa for the series of mercaptoazulenes in Chapter 1, Figure 11.

Compound	HA_{DMSO} (kcals/mol)	A^-_{DMSO} (kcals/mol)	HA_{gas} (kcals/mol)	A^-_{gas} (kcals/mol)	Calc. pKa (DMSO)
2-mercapto-1,3-dimethoxycarbonylazulene	-12.13	-58.33	-780,809.03	-780,474.21	10.73
6-mercapto-1,3-dimethoxycarbonylazulene	-12.64	-48.07	-780,813.62	-780,497.50	4.92
2-mercaptoazulene	-5.91	-52.06	-493,765.74	-493,434.40	8.21
6-mercaptoazulene	-5.96	-49.33	-493,763.19	-493,436.72	6.68
2,6-dimercaptoazulene (6-SH pKa)	-7.1	-46.58	-744,602.24	-744,277.80	8.04
2,6-dimercaptoazulene (2-SH pKa)	-7.1	-49.92	-744,602.24	-744,273.05	9.08
[2-mercapto-6-thiolateazulene]$^{-1}$	-46.58	-161.97	-744,277.80	-743,873.09	11.24
2,6-dimercapto-1,3-dimethoxycarbonylazulene (6-SH pKa)	-13.64	-48.19	-1,031,645.46	-1,031,330.66	4.58
2,6-dimercapto-1,3-dimethoxycarbonylazulene (2-SH pKa)	-13.64	-55.73	-1,031,645.46	-1,031,312.12	12.65
[2-mercapto-6-thiolate-1,3-dimethoxycarbonylazulene]$^{-1}$	-48.19	-158.6	-1,031,330.66	-1,030,924.35	16.06
2-mercapto-1,3-dimethoxycarbonyl-2',6-biazulene	-14.12	-56.49	-1,022,984.82	-1,022,654.62	10.14
2-mercapto-6-[thiolate-gold(I)-PMe3]-1,3-dimethoxycarbonyl-azulene	-19.11	-66.67	-13,770,567.15	-13,770,225.36	14.83
[Na][2-mercapto-6-thiolate-1,3-dimethoxycarbonyl-azulene]	-39.48	-83.05	-1,133,526.65	-1,133,188.26	15.27

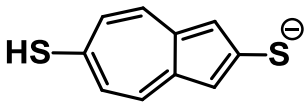
Appendix 2. Supplementary Information for Chapter 2

Table A2.1. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-6-azulenethiolate anion.



Atom	x	y	z
C	0.134537	0.132992	0.007379
H	-0.832694	0.439687	-0.365331
C	1.367558	0.356796	-0.627131
C	2.404983	-0.171989	0.160281
C	1.825685	-0.757804	1.301112
C	2.515286	-1.421958	2.336757
C	2.049074	-2.048984	3.466577
C	0.712909	-2.225465	3.956279
C	-0.452687	-1.709586	3.298886
C	-0.585002	-0.999144	2.130308
C	0.384438	-0.562333	1.205175
H	-1.608079	-0.733064	1.866738
H	-1.374058	-1.935578	3.823857
S	0.498485	-3.107384	5.419573
H	2.800299	-2.499090	4.105998
H	3.597346	-1.449983	2.213483
H	3.460177	-0.138764	-0.073382
S	1.575367	1.221452	-2.183007
H	1.608544	0.147811	-3.013425

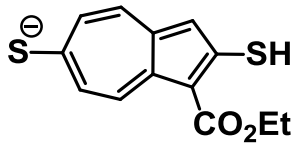
Table A2.2. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-2-azulenethiolate anion.



Atom	x	y	z
C	0.015712	0.049779	0.016326
H	-0.954444	0.378830	-0.329689
C	1.229748	0.235724	-0.724515
C	2.280263	-0.324694	0.076981
C	1.762526	-0.846945	1.247134
C	2.475414	-1.485763	2.272403
C	2.015952	-2.056940	3.452777
C	0.709236	-2.145199	3.951799
C	-0.470240	-1.638583	3.386163
C	-0.658354	-0.966070	2.185671
C	0.276705	-0.600554	1.206931
H	-1.684294	-0.677273	1.968617
H	-1.368787	-1.805720	3.970901
S	0.533534	-2.977669	5.560830

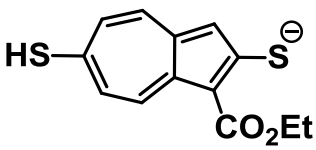
H	0.212431	-4.221587	5.120984
H	2.777961	-2.507665	4.079792
H	3.548941	-1.557236	2.112760
H	3.321251	-0.335749	-0.216360
S	1.384567	0.969300	-2.255639

Table A2.3. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-1-ethoxycarbonyl-6-azulenethiolate anion.



Atom	x	y	z
C	0.405582	0.935826	-0.980775
C	-7.021987	1.126369	0.523276
C	-4.134797	-0.205324	0.845208
C	-4.808968	1.925790	-0.354914
C	-3.926088	0.961514	0.079678
C	-6.218176	2.076565	-0.188342
C	-3.861019	-2.159168	2.045085
C	-6.668438	-0.025014	1.173956
C	-3.154523	-1.167921	1.287130
C	-1.731964	-1.199756	1.069807
C	0.156257	-0.152916	0.043354
C	-5.409619	-0.644982	1.349155
C	-5.209715	-1.840260	2.075703
H	0.469719	-1.131857	-0.325510
H	-0.151001	0.734210	-1.897888
H	0.093040	1.909264	-0.597045
O	-0.944619	-2.048781	1.491480
S	-3.214162	-3.604795	2.849335
H	-4.364182	2.728021	-0.934007
H	-1.929564	-3.358476	2.483848
S	-6.987477	3.459154	-0.860636
H	-5.983140	-2.406573	2.575442
H	-8.075585	1.382012	0.545693
H	0.703180	0.038597	0.971279
H	-7.492762	-0.556704	1.646587
O	-1.252175	-0.164392	0.309398
H	-2.901156	1.134043	-0.215920
H	1.469337	0.986559	-1.228376

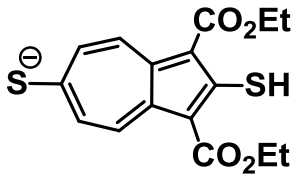
Table A2.4. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-1-ethoxycarbonyl-2-azulenethiolate anion.



Atom	x	y	z
C	-0.000405	-0.019360	-0.060946

O	-1.376588	-0.127026	0.308213
C	-1.695295	-1.074836	1.226246
C	-3.124763	-1.156428	1.495676
C	-4.222553	-0.654774	0.679859
C	-5.417063	-0.915058	1.427691
H	-6.400198	-0.634649	1.076857
C	-5.133564	-1.566758	2.604055
C	-3.655709	-1.759242	2.661089
C	-2.957621	-2.415305	3.672936
C	-3.440269	-3.051407	4.825715
C	-4.734255	-3.170364	5.314025
C	-5.919136	-2.646259	4.752473
C	-6.085624	-1.960631	3.570842
H	-7.106893	-1.666659	3.340555
H	-6.821170	-2.815554	5.331049
S	-4.912386	-4.048134	6.896260
H	-5.532766	-5.163787	6.436056
H	-2.677614	-3.536741	5.426272
H	-1.887367	-2.473601	3.525697
S	-4.246990	0.041566	-0.870793
O	-0.819521	-1.743016	1.762393
C	0.062687	0.974765	-1.203101
H	1.096453	1.115430	-1.532346
H	-0.341319	1.940002	-0.891788
H	-0.533489	0.619842	-2.044514
H	0.588421	0.313148	0.800062
H	0.383358	-1.000465	-0.354087

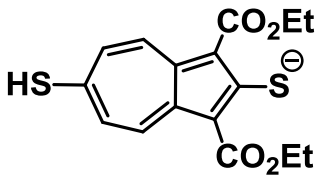
Table A2.5. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate anion.



Atom	x	y	z
C	0.181844	-0.028039	0.139241
C	-1.075743	-0.583194	0.775431
H	-1.117057	-1.670000	0.678282
H	-1.952672	-0.160429	0.278078
H	-1.127367	-0.323697	1.835006
O	1.314495	-0.557489	0.846626
C	2.544055	-0.170676	0.381240
C	3.663388	-0.584693	1.197811
C	5.020372	-0.241027	0.918907
C	5.852094	-0.827344	1.897744
C	5.014473	-1.555757	2.812465
C	5.480988	-2.276942	3.940265
C	4.809142	-3.010169	4.883214
C	3.413820	-3.271011	5.057560
C	2.424705	-2.714159	4.186380

C	2.529775	-1.923852	3.068415
C	3.660235	-1.394478	2.397674
H	1.582648	-1.660381	2.622931
H	1.412152	-2.978382	4.472197
S	2.912572	-4.268805	6.358900
H	5.430455	-3.480532	5.637628
H	6.556813	-2.257111	4.057820
C	7.299855	-0.743606	2.007799
O	7.830403	0.267779	1.253808
C	9.255837	0.418225	1.283295
C	9.579443	1.799351	0.745396
H	10.657950	1.974732	0.795954
H	9.078115	2.563332	1.340517
H	9.249682	1.907853	-0.289394
H	9.614254	0.290649	2.305595
H	9.713854	-0.369053	0.676787
O	8.021319	-1.451199	2.692646
S	5.607890	0.718670	-0.453158
H	4.368720	0.834721	-0.998632
O	2.599448	0.485454	-0.658723
H	0.205391	1.063712	0.199623
H	0.247989	-0.304785	-0.914825

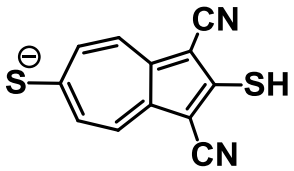
Table A2.6. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate anion.



Atom	x	y	z
C	0.449340	-0.032080	-0.184010
C	0.735282	0.271877	-1.644019
H	1.552286	0.989549	-1.724255
H	-0.155394	0.688055	-2.125330
H	1.035714	-0.630648	-2.179936
O	1.651593	-0.571166	0.382416
C	1.859631	-0.407049	1.706734
C	3.226915	-0.751381	2.117409
C	4.451567	-0.503336	1.374358
C	5.525411	-1.017981	2.209593
C	4.988850	-1.595408	3.371662
C	5.706205	-2.244227	4.387960
C	5.259231	-2.838728	5.562085
C	3.967504	-2.927663	6.082890
C	2.793250	-2.407910	5.524722
C	2.597957	-1.745793	4.323482
C	3.523923	-1.378038	3.332122
H	1.579474	-1.437132	4.124833
H	1.897138	-2.547770	6.120201
S	3.815073	-3.753190	7.696060

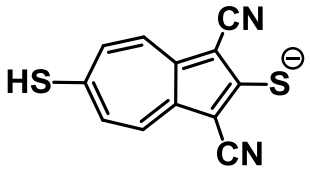
H	3.174086	-4.873156	7.280019
H	6.032393	-3.311268	6.158837
H	6.770199	-2.323420	4.207269
C	6.965901	-0.960797	1.946944
O	7.323916	0.123423	1.224992
C	8.674670	0.204165	0.758257
C	8.683142	1.224609	-0.363228
H	9.697021	1.360640	-0.751227
H	8.310981	2.187338	-0.007192
H	8.031434	0.895115	-1.172865
H	9.329016	0.502484	1.584139
H	9.006164	-0.779312	0.417735
O	7.799301	-1.764554	2.342820
S	4.582736	0.237533	-0.145284
O	0.968532	-0.029411	2.452765
H	-0.356878	-0.765108	-0.072406
H	0.156229	0.861620	0.369601

Table A2.7. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-1,3-dicyano-6-azulenethiolate anion.



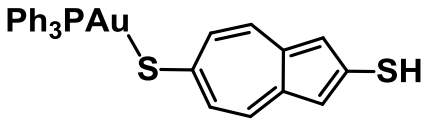
Atom	x	y	z
C	-0.088193	-0.024921	-0.078622
C	-1.378457	0.381353	-0.472260
N	-2.444207	0.709372	-0.789181
C	1.090091	0.107895	-0.837217
C	2.160684	-0.430005	-0.091738
C	1.644382	-0.922338	1.148456
C	2.403730	-1.552209	2.159093
C	2.012763	-2.076413	3.362314
C	0.721677	-2.145537	3.987098
C	-0.471786	-1.619001	3.383013
C	-0.674279	-0.988230	2.183494
C	0.242095	-0.665832	1.158693
H	-1.700068	-0.688063	1.984236
H	-1.355331	-1.756361	3.995955
S	0.602095	-2.886949	5.523617
H	2.799610	-2.521443	3.960552
H	3.464854	-1.643200	1.940550
C	3.503403	-0.472241	-0.508375
N	4.604619	-0.500258	-0.873227
S	1.157118	0.828520	-2.453803
H	2.466311	0.561601	-2.661559

Table A2.8. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-1,3-dicyano-2-azulenethiolate anion.



Atom	x	y	z
C	0.007975	0.011182	-0.046508
C	-1.293514	0.383883	-0.446230
N	-2.384679	0.662669	-0.716185
C	1.218026	0.227127	-0.810163
C	2.276971	-0.320845	0.010474
C	1.754724	-0.866400	1.190407
C	2.480616	-1.514229	2.196917
C	2.029985	-2.113966	3.366770
C	0.734171	-2.196119	3.885423
C	-0.442998	-1.671221	3.336292
C	-0.639070	-1.004053	2.137078
C	0.292813	-0.644794	1.155017
H	-1.662476	-0.708531	1.926990
H	-1.336606	-1.812144	3.934700
S	0.583457	-3.030024	5.494086
H	-0.121486	-4.110877	5.079303
H	2.797332	-2.595121	3.963332
H	3.550534	-1.580381	2.023882
C	3.649592	-0.329052	-0.319201
N	4.787256	-0.364613	-0.534776
S	1.351270	0.948559	-2.323341

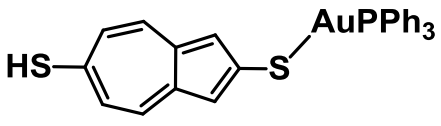
Table A2.9. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](2-mercapto-6-azulenethiolate).



Atom	x	y	z
H	2.002766	-2.119427	-0.270296
C	2.965590	-2.486417	0.078883
C	4.144933	-1.722566	0.230365
C	5.190476	-2.545401	0.704940
C	4.681912	-3.848948	0.863078
C	5.396017	-4.966674	1.312485
C	4.974846	-6.279522	1.515955
C	3.701917	-6.861672	1.315683
C	-1.936978	-8.503574	2.266787
C	-3.161253	-8.754450	1.630403
C	-4.055840	-7.704911	1.396821
C	-3.735447	-6.405205	1.797744
C	-2.512525	-6.150957	2.428533
C	-1.611767	-7.192822	2.656341

C	-1.279503	-11.313149	1.656175
C	-2.219441	-12.217594	2.173991
C	-2.634799	-13.309550	1.406623
C	-2.113747	-13.506091	0.124194
C	-1.171438	-12.611034	-0.392000
C	-0.751012	-11.519683	0.371490
C	2.544225	-6.216698	0.823229
C	2.355680	-4.885409	0.459504
C	3.252819	-3.810164	0.462216
H	6.211749	-2.231814	0.911371
C	-0.963996	-10.282998	4.387001
C	-2.152493	-9.979270	5.068092
C	-2.306667	-10.354624	6.406300
C	-1.279352	-11.032315	7.069049
C	-0.090378	-11.329708	6.394584
C	0.071387	-10.951918	5.060378
H	-2.952696	-9.439608	4.559419
S	3.664582	-8.614642	1.701281
Au	1.450297	-9.190643	2.114984
P	-0.704357	-9.837813	2.610496
H	-0.649475	-6.988097	3.130058
H	-2.253115	-5.136768	2.734851
H	-4.434168	-5.588095	1.611922
H	-5.004238	-7.906244	0.896653
H	-3.414352	-9.765221	1.308728
H	0.001322	-10.830946	-0.020410
H	-0.752744	-12.767557	-1.386762
H	-2.435609	-14.362801	-0.469872
H	-3.362637	-14.012237	1.815716
H	-2.618333	-12.077618	3.179772
H	1.346278	-4.643325	0.108577
H	1.670031	-6.861909	0.707221
H	5.737080	-6.960197	1.902758
H	6.447706	-4.778147	1.553557
S	4.224355	0.009277	-0.148167
H	5.516408	0.185515	0.239642
H	1.009112	-11.162591	4.541496
H	0.719703	-11.845844	6.911833
H	-1.400861	-11.320675	8.114063
H	-3.230967	-10.110246	6.932263

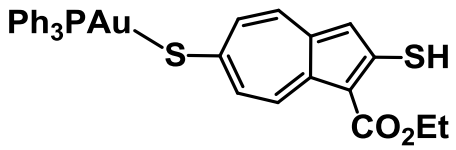
Table A2.10. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](6-mercapto-2-azulenethiolate).



Atom	x	y	z
H	4.052840	-1.020154	-1.040053
C	4.587370	-0.648843	-0.168187
C	5.642903	0.299199	-0.197564

C	6.092195	0.521799	1.130789
C	5.331919	-0.271922	2.003194
C	5.467960	-0.334314	3.393738
C	4.760644	-1.087913	4.332808
C	3.707247	-1.996765	4.122870
C	3.108994	-2.374807	2.905372
C	3.400369	-1.946810	1.609880
C	4.357637	-1.029605	1.162510
H	6.892389	1.200000	1.420754
C	4.828607	0.400767	-6.901148
C	4.776696	-0.421277	-8.036838
C	5.467634	-0.055117	-9.196541
C	6.210311	1.128439	-9.228827
C	6.269417	1.946829	-8.095534
C	5.587161	1.582978	-6.932925
C	3.529199	-1.811121	-5.460398
C	2.318755	-2.280831	-5.992582
C	2.076808	-3.656054	-6.071137
C	3.037433	-4.565668	-5.619516
C	4.242956	-4.100388	-5.082980
C	4.487164	-2.728384	-4.996173
C	2.302579	0.863593	-5.476777
C	1.753676	1.234736	-6.714013
C	0.515588	1.882954	-6.764204
C	-0.178752	2.164538	-5.583964
C	0.368912	1.802150	-4.348908
C	1.607856	1.160096	-4.292659
H	2.296680	1.029823	-7.637924
S	2.980368	-2.833868	5.545405
H	3.733213	-2.220901	6.497153
H	2.783634	-2.396515	0.825026
H	2.298703	-3.105892	2.983386
H	5.077564	-0.947023	5.369091
H	6.251701	0.305445	3.812831
S	6.371633	1.119793	-1.578553
Au	5.114232	0.522544	-3.439218
P	3.927677	-0.008782	-5.339369
H	5.650217	2.210939	-6.041467
H	6.856602	2.866002	-8.111999
H	6.750375	1.409416	-10.134056
H	5.427634	-0.700707	-10.075416
H	4.207274	-1.351234	-8.014407
H	5.417368	-2.363106	-4.555618
H	4.990223	-4.806124	-4.717820
H	2.843532	-5.637983	-5.677769
H	1.131596	-4.015883	-6.480272
H	1.560579	-1.575176	-6.335092
H	2.047902	0.902137	-3.327225
H	-0.162275	2.031272	-3.424280
H	-1.142523	2.673638	-5.625534
H	0.097622	2.174078	-7.728860

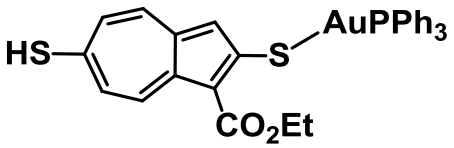
Table A2.11. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1-ethoxycarbonyl-2-mercapto-6-azulenethiolate).



Atom	x	y	z
C	-0.121847	0.245355	0.311400
C	0.686216	-0.835896	1.003912
H	1.685714	-0.447601	1.245462
H	0.808223	-1.716189	0.358844
H	0.207437	-1.151062	1.940332
O	-1.434692	-0.312166	0.015491
C	-2.311179	0.536350	-0.606630
C	-3.618674	-0.033913	-0.883260
C	-4.675358	0.703902	-1.525665
C	-5.808831	-0.115296	-1.642785
H	-6.756956	0.177686	-2.088634
C	-5.518567	-1.374499	-1.088756
C	-4.128162	-1.346983	-0.602688
C	-3.460215	-2.416456	0.005172
C	-3.908502	-3.703437	0.319393
C	-5.158652	-4.318207	0.114064
C	-6.281953	-3.728051	-0.517682
C	-6.425866	-2.449428	-1.031500
H	-7.406085	-2.238066	-1.472084
H	-7.154719	-4.378127	-0.617053
S	-5.229177	-6.017934	0.675616
Au	-7.470084	-6.537503	1.023651
P	-9.655180	-7.121364	1.461936
C	-10.846035	-5.792027	0.980603
C	-12.043336	-6.062986	0.302587
C	-12.907307	-5.016112	-0.035628
C	-12.583596	-3.699564	0.302498
C	-11.387346	-3.425854	0.975270
C	-10.516925	-4.465292	1.307864
H	-9.575163	-4.246530	1.815078
H	-11.125190	-2.399041	1.233586
H	-13.258288	-2.885008	0.035494
H	-13.834796	-5.233473	-0.567206
H	-12.298895	-7.087510	0.030253
C	-10.212163	-8.643436	0.573725
C	-11.166371	-9.518758	1.114483
C	-11.565060	-10.648526	0.394375
C	-11.014503	-10.910716	-0.863563
C	-10.058193	-10.044290	-1.402397
C	-9.653033	-8.916457	-0.685541
H	-8.889033	-8.250661	-1.094045
H	-9.616911	-10.251758	-2.377807

H	-11.324012	-11.796381	-1.420331
H	-12.303640	-11.328757	0.821536
H	-11.589576	-9.326407	2.101292
C	-9.996438	-7.446855	3.249677
C	-11.222496	-7.116149	3.846879
C	-11.440766	-7.400934	5.198371
C	-10.439919	-8.013766	5.957964
C	-9.213809	-8.337183	5.367202
C	-8.988731	-8.051155	4.019247
H	-8.023544	-8.282849	3.563976
H	-8.424794	-8.802006	5.959998
H	-10.611502	-8.230705	7.013251
H	-12.393862	-7.136185	5.658632
H	-12.001586	-6.625224	3.261831
H	-3.168409	-4.331932	0.821847
H	-2.429255	-2.212203	0.291663
S	-4.636426	2.364727	-2.101295
H	-3.328478	2.525374	-1.673890
O	-1.962907	1.694981	-0.885881
H	0.345300	0.570976	-0.628896
H	-0.248972	1.134378	0.945365

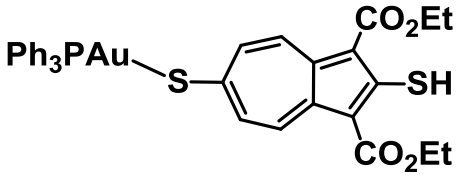
Table A2.12. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1-ethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
C	5.221211	5.143500	-6.555233
C	4.961060	6.324797	-7.266418
C	3.720047	6.510364	-7.884095
C	2.736519	5.521191	-7.796415
C	2.991616	4.343947	-7.084738
C	4.226396	4.155868	-6.460762
C	7.646402	6.484122	-5.572206
C	8.604017	6.947755	-6.486108
C	9.180890	8.210359	-6.313913
C	8.803414	9.015333	-5.235711
C	7.850559	8.554563	-4.320620
C	7.279279	7.290997	-4.481275
C	7.850979	3.902593	-6.968228
C	7.579357	3.958580	-8.344001
C	8.381085	3.250988	-9.244625
C	9.456418	2.488136	-8.779202
C	9.726526	2.425791	-7.408112
C	8.923731	3.123824	-6.503372
C	7.703060	2.995304	-0.682498

C	8.761583	3.863332	-1.035666
C	9.699048	3.910879	0.002846
C	9.210129	3.022590	1.079337
C	7.971987	2.466381	0.632692
C	7.176283	1.522702	1.422453
C	5.203590	0.181065	1.498113
C	4.012206	-0.140628	0.616029
C	9.845493	2.777687	2.299189
C	11.051638	3.283166	2.801414
C	11.960203	4.177326	2.219705
C	11.872851	4.798707	0.953284
C	10.880377	4.673643	-0.008361
H	9.312806	2.085483	2.954886
P	6.841638	4.826222	-5.724224
H	4.417069	3.246293	-5.887554
H	2.222794	3.573885	-7.004207
H	1.767838	5.669909	-8.275443
H	3.521881	7.433758	-8.430276
H	5.721647	7.104921	-7.329218
H	6.554351	6.921608	-3.752301
H	7.560667	9.174333	-3.470965
H	9.257344	9.998159	-5.102868
H	9.930678	8.561866	-7.024562
H	8.907398	6.321602	-7.326153
H	9.118156	3.053688	-5.430671
H	10.556858	1.822151	-7.038797
H	10.078657	1.934408	-9.483740
H	8.160759	3.293480	-10.312599
H	6.735175	4.543552	-8.712352
Au	6.633271	3.758857	-3.689027
S	6.296870	2.631324	-1.678111
H	8.824666	4.409944	-1.974325
O	7.460233	1.102712	2.544186
O	6.036609	1.126212	0.776657
H	3.355663	-0.857667	1.130917
H	3.430728	0.763746	0.393185
H	4.334618	-0.586332	-0.334001
H	5.799211	-0.714364	1.729919
H	4.899559	0.630843	2.454939
H	11.039729	5.260002	-0.919297
H	12.699026	5.466349	0.692692
S	13.446629	4.643474	3.121811
H	13.193058	3.909379	4.238144
H	11.312460	2.915338	3.796854

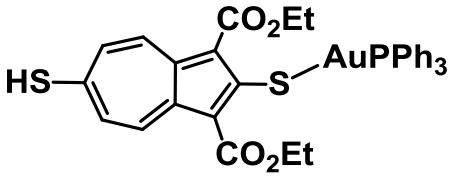
Table A2.13. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate) (II.10).



Atom	x	y	z
C	0.167696	-0.127384	-0.251053
C	1.531772	-2.036456	0.211604
C	2.897538	-2.521989	0.425184
C	4.104829	-1.762494	0.448138
C	5.209460	-2.645061	0.710579
C	4.679791	-3.974063	0.855066
C	5.403254	-5.150711	1.128562
C	4.977028	-6.462903	1.312539
C	3.681413	-7.023412	1.262101
C	-1.971238	-8.677273	1.849501
C	-3.159235	-9.051072	1.204170
C	-4.031478	-8.068401	0.724121
C	-3.723535	-6.714787	0.884218
C	-2.537988	-6.338535	1.525730
C	-1.662425	-7.314825	2.004175
C	-1.271568	-11.539349	1.767799
C	-2.149400	-12.415162	2.424026
C	-2.510564	-13.623634	1.820440
C	-2.000130	-13.962567	0.564238
C	-1.120262	-13.094124	-0.090142
C	-0.750397	-11.889298	0.510710
C	2.503186	-6.309641	0.949297
C	2.316949	-4.956378	0.705055
C	3.235028	-3.889748	0.672993
C	6.594291	-2.197067	0.806391
C	8.892454	-2.766671	1.147824
C	9.729600	-4.001459	1.415152
C	0.338631	1.360542	-0.489068
C	-1.121989	-10.051751	4.303821
C	-2.375698	-9.717601	4.839217
C	-2.607397	-9.852122	6.211514
C	-1.592349	-10.316968	7.053086
C	-0.339347	-10.643318	6.523233
C	-0.101241	-10.507132	5.154038
O	1.490321	-0.692381	-0.043355
S	3.636064	-8.778026	1.585489
Au	1.412089	-9.334670	2.011860
P	-0.764680	-9.918366	2.495697
H	-0.731324	-7.017452	2.490742
H	-2.283843	-5.283804	1.639172
H	-4.401384	-5.950933	0.501234
H	-4.951286	-8.365628	0.218403
H	-3.399752	-10.105958	1.065717
H	-0.046223	-11.220314	0.010419
H	-0.711362	-13.359315	-1.065611
H	-2.281431	-14.907937	0.098469
H	-3.189205	-14.303765	2.337651
H	-2.543406	-12.160137	3.408257
H	1.287221	-4.653420	0.504054

H	1.596150	-6.918035	0.896640
H	5.774527	-7.172637	1.548132
H	6.477991	-5.009500	1.228203
O	7.502952	-3.193529	1.045550
H	9.179754	-2.269138	0.210315
H	8.977166	-2.027393	1.957292
H	10.787639	-3.714209	1.498075
H	9.636185	-4.730770	0.598668
H	9.434320	-4.487447	2.355271
O	6.985770	-1.026183	0.690241
S	4.204588	-0.027027	0.198318
H	5.578748	-0.050908	0.381160
O	0.505405	-2.715549	0.248606
H	-0.302484	-0.631962	-1.108440
H	-0.449879	-0.334832	0.635394
H	-0.646338	1.822309	-0.648846
H	0.957551	1.550383	-1.375948
H	0.811735	1.846981	0.374296
H	0.883329	-10.739564	4.742892
H	0.459396	-10.992920	7.178710
H	-1.774737	-10.416122	8.124298
H	-3.581632	-9.585096	6.623443
H	-3.165610	-9.339931	4.188270

Table A2.14. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).

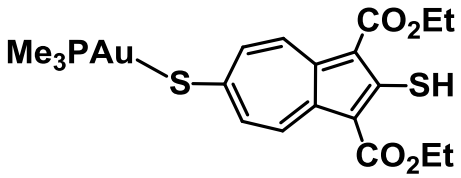


Atom	x	y	z
C	1.107587	2.009710	-0.717105
O	2.195533	1.257169	-0.112141
C	3.431318	1.452404	-0.645996
C	4.462107	0.648989	0.037576
C	4.599837	0.396302	1.436381
C	5.630025	-0.582563	1.615230
C	6.175572	-0.895852	0.336502
C	7.219247	-1.796312	0.085635
C	7.826440	-2.156256	-1.117510
C	7.543309	-1.722941	-2.423559
S	8.506902	-2.369079	-3.795235
H	9.330206	-3.159088	-3.054537
C	6.555987	-0.801436	-2.826086
C	5.638511	-0.099620	-2.051650
C	5.440864	-0.103086	-0.661337
H	4.984887	0.579892	-2.603376
H	6.503920	-0.600775	-3.900396
H	8.635156	-2.885116	-1.016517
H	7.629676	-2.270196	0.979250

C	6.107283	-1.184125	2.869349
O	5.169611	-1.135901	3.858086
C	5.588571	-1.659192	5.148781
H	5.874960	-2.714056	5.027581
H	6.481777	-1.109666	5.480165
C	4.425796	-1.488328	6.107354
H	4.705647	-1.874210	7.098371
H	3.542794	-2.040108	5.759334
H	4.153809	-0.430077	6.210233
O	7.207435	-1.708175	3.035053
S	3.772842	1.236779	2.753891
Au	3.778018	3.464688	2.064165
P	3.911066	5.719921	1.599338
C	3.207826	6.746908	2.967829
C	3.800251	7.947451	3.387423
C	3.223047	8.687468	4.424217
C	2.054670	8.236511	5.044538
C	1.463862	7.037448	4.632201
C	2.040588	6.290451	3.603113
H	1.593834	5.342365	3.297180
H	0.558363	6.675553	5.120618
H	1.608881	8.813987	5.855729
H	3.691613	9.617258	4.749352
H	4.717129	8.300163	2.913990
C	5.653670	6.302465	1.390037
C	5.977529	7.394625	0.570016
C	7.305863	7.816159	0.459213
C	8.315229	7.149022	1.159712
C	7.997170	6.054287	1.969700
C	6.671641	5.628204	2.083401
H	6.423619	4.759252	2.696997
H	8.783480	5.521133	2.505313
H	9.351928	7.476050	1.066040
H	7.552273	8.663889	-0.182079
H	5.195502	7.907509	0.008078
C	3.042438	6.283867	0.067657
C	2.281998	7.462729	0.030737
C	1.664449	7.858731	-1.160262
C	1.803146	7.082558	-2.314707
C	2.554635	5.903154	-2.276843
C	3.169101	5.496893	-1.090068
H	3.729109	4.559760	-1.072543
H	2.656317	5.283329	-3.168487
H	1.319756	7.392595	-3.242349
H	1.072705	8.775232	-1.182444
H	2.166538	8.068779	0.930219
O	3.624124	2.159651	-1.634839
H	1.292318	3.082854	-0.558618
H	1.107271	1.825860	-1.801585
C	-0.178495	1.552233	-0.056559
H	-1.028623	2.105720	-0.480051

H	-0.149414	1.732080	1.026135
H	-0.346734	0.480055	-0.225154

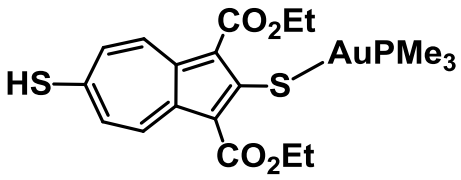
Table A2.15. Cartesian coordinates (Å) for the optimized structure of [Me_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate).



Atom	x	y	z
C	0.047406	0.055711	-0.123799
C	0.240323	1.511822	-0.501929
H	-0.739176	1.975951	-0.686743
H	0.845265	1.606404	-1.413255
H	0.738634	2.066478	0.304275
O	1.364243	-0.512268	0.113585
C	1.388332	-1.829619	0.483331
C	2.751492	-2.320640	0.706210
C	3.976119	-1.601156	0.572344
C	5.071714	-2.476388	0.892454
C	4.518773	-3.759512	1.229504
C	5.228450	-4.915967	1.605034
C	4.783976	-6.189838	1.944521
C	3.475309	-6.716745	2.020369
C	2.294211	-5.993612	1.743482
C	2.126415	-4.672889	1.351939
C	3.068650	-3.655056	1.111303
H	1.092471	-4.356097	1.199384
H	1.367800	-6.564039	1.854941
S	3.422556	-8.431419	2.507789
Au	1.194312	-9.100317	2.610805
P	-0.957317	-9.887106	2.775227
C	-2.252482	-8.591966	2.529849
H	-2.121499	-7.800206	3.278092
H	-2.140043	-8.146184	1.533631
H	-3.258160	-9.024181	2.625609
C	-1.402993	-11.204326	1.556122
H	-0.730779	-12.061543	1.685091
H	-2.443351	-11.529729	1.694389
H	-1.272774	-10.813926	0.539040
C	-1.378772	-10.636754	4.413187
H	-0.708003	-11.482372	4.607996
H	-1.229952	-9.888998	5.201925
H	-2.420950	-10.984375	4.426885
H	5.578524	-6.897751	2.195529
H	6.309873	-4.795235	1.634358
C	6.470742	-2.064233	0.859855
O	7.364560	-3.046467	1.193289
C	8.768498	-2.656895	1.168248
C	9.584293	-3.873364	1.559679

H	10.653131	-3.614814	1.551066
H	9.427526	-4.701753	0.855348
H	9.325746	-4.218257	2.569930
H	9.019161	-2.300268	0.159256
H	8.916075	-1.819073	1.864504
O	6.884503	-0.933288	0.564331
S	4.104400	0.082521	0.091303
H	5.486000	0.037287	0.195895
O	0.352276	-2.483210	0.603043
H	-0.446743	-0.517280	-0.922560
H	-0.556928	-0.057553	0.788071

Table A2.16. Cartesian coordinates (Å) for the optimized structure of [Me_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
C	-0.056394	0.203204	0.505974
O	1.044087	-0.633991	0.951630
C	2.264154	-0.363272	0.409890
C	3.309028	-1.255413	0.951044
C	3.555855	-1.590728	2.316662
C	4.549994	-2.623072	2.349138
C	4.960871	-2.889626	1.010473
C	5.929235	-3.820907	0.614443
C	6.404989	-4.137711	-0.658810
C	6.027680	-3.617332	-1.907539
S	6.829197	-4.225113	-3.396481
H	7.633082	-5.137026	-2.785585
C	5.058066	-2.627350	-2.166920
C	4.253051	-1.930213	-1.273522
C	4.181373	-2.007881	0.127062
H	3.588129	-1.190591	-1.726268
H	4.918085	-2.364209	-3.219427
H	7.183114	-4.905917	-0.672960
H	6.393387	-4.364674	1.439158
C	5.108150	-3.313240	3.521179
O	4.295396	-3.223536	4.612088
C	4.807333	-3.828838	5.831127
H	4.967331	-4.902513	5.653649
H	5.785260	-3.382540	6.064459
C	3.788418	-3.575161	6.925550
H	4.139905	-4.021505	7.866893
H	2.817740	-4.022284	6.673488
H	3.642193	-2.498963	7.083772
O	6.169011	-3.935508	3.545104
S	2.887660	-0.775975	3.736838

Au	2.817427	1.439896	3.008182
P	2.898156	3.596090	2.223146
C	1.266454	4.436227	1.977802
H	0.730477	4.482055	2.933896
H	1.406997	5.453428	1.586064
H	0.667243	3.853057	1.267889
C	3.854476	4.804251	3.249022
H	3.382618	4.898989	4.234746
H	4.875427	4.428814	3.389055
H	3.888526	5.788996	2.762492
C	3.693931	3.669498	0.558475
H	4.744452	3.367253	0.651069
H	3.192364	2.953462	-0.105945
H	3.637527	4.684912	0.141711
O	2.426206	0.468605	-0.481743
H	0.135082	1.234013	0.844264
H	-0.080690	0.209452	-0.593274
C	-1.328444	-0.360463	1.109384
H	-2.188251	0.251460	0.800451
H	-1.275878	-0.362738	2.205901
H	-1.499719	-1.390045	0.768640

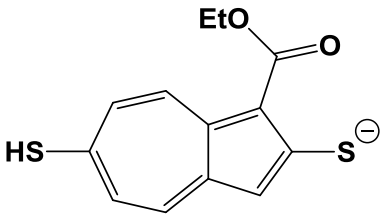
Table A2.17. TDDFT-calculated optical transitions for the lower energy portion of the electronic excitation spectrum of II.10.

Calc. Transition (nm)	Calc. Transition w/ 35nm Offset (nm)	Oscillator Strength	Composition (%)	Experimental Transition (nm)
410	445	0.3756	70.6% HOMO→LUMO	445
			9.7% HOMO→LUMO+3	
			5.2% HOMO-1→LUMO+1	
			4.9% HOMO-1→LUMO	
			4.1% HOMO-1→LUMO+2	
			1.1% HOMO→LUMO+8	
		0.0031	56.8% HOMO→LUMO+1	
			37.1% HOMO→LUMO+2	
			2.8% HOMO-1→LUMO	
380	415	0.0224	41.6% HOMO→LUMO+3	425
			10.0% HOMO-1→LUMO	
			9.2% HOMO→LUMO+1	
			9.2% HOMO→LUMO+2	
			5.1% HOMO-1→LUMO+1	
			3.5% HOMO-1→LUMO+2	
			2.4% HOMO→LUMO	

			1.0% HOMO-2→LUMO	
		0.0435	43.5% HOMO→LUMO+3	
			24.7% HOMO-1→LUMO	
			18.7% HOMO→LUMO+2	
			4.5% HOMO→LUMO+1	
			1.5% HOMO→LUMO+4	
		0.0042	94.7% HOMO→LUMO+4	
			1.2% HOMO→LUMO+5	
			1.0% HOMO-1→LUMO	
		0.0015	96.7% HOMO→LUMO+5	
			1.5% HOMO→LUMO+4	
332	367	0.0312	56.5% HOMO-1→LUMO+1	365
			40.7% HOMO-1→LUMO+2	
		0.0034	64.8% HOMO→LUMO+6	
			22.9% HOMO→LUMO+7	
			3.6% HOMO→LUMO+9	
			2.3% HOMO-1→LUMO+3	
			1.3% HOMO-2→LUMO+1	
		0.0334	81.6% HOMO-1→LUMO+3	
			5.4% HOMO→LUMO+7	
			5.2% HOMO-1→LUMO+2	
			1.9% HOMO-1→LUMO	
			1.5% HOMO-1→LUMO+1	
			1.1% HOMO-1→LUMO+4	

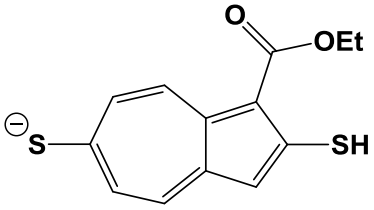
Table A2.18. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of 6-mercapto-1-ethoxycarbonyl-2-azulenethiolate anion

Atom	x	y	z
C	0.127064	-0.039045	0.054001
C	-1.689452	-0.990697	1.288554
C	-3.146231	-1.106468	1.353423
C	-3.849707	-2.212290	1.981988
C	-5.241994	-1.881141	1.915229
C	-5.432421	-0.674301	1.285274
C	-4.082949	-0.153550	0.903423
C	-3.840163	1.069549	0.273416
C	-4.735006	2.063040	-0.137255
C	-6.122630	2.113422	-0.071976
C	-6.995286	1.124546	0.426604
C	-6.686297	-0.075070	1.031054
C	0.351362	0.669099	-1.270859
O	-1.270122	-0.341173	0.140042



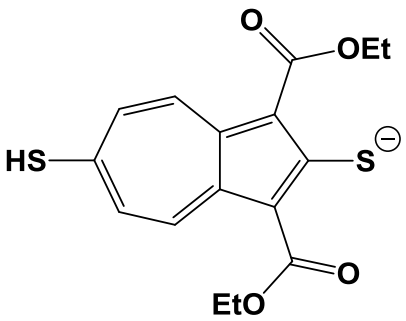
H	-6.017896	-2.525925	2.303012
H	-7.538699	-0.661273	1.366078
H	-8.052972	1.345882	0.330556
S	-6.897133	3.602746	-0.771623
H	-7.294861	4.188310	0.385676
H	-4.266390	2.935226	-0.581526
H	-2.801719	1.286864	0.066365
S	-3.251100	-3.664496	2.618166
O	-0.883343	-1.375963	2.105562
H	1.403584	0.946773	-1.380724
H	-0.249856	1.577381	-1.335252
H	0.072926	0.020691	-2.103905
H	0.419616	0.591561	0.899125
H	0.710672	-0.959698	0.124575

Table A2.19. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of 2-mercapto-1-ethoxycarbonyl-6-azulenethiolate anion.



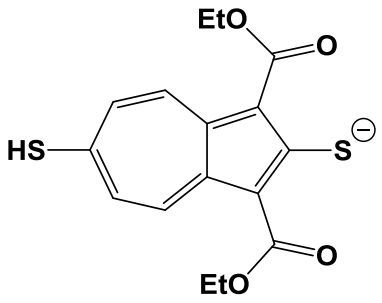
Atom	x	y	z
C	0.029136	0.716015	-1.376930
C	-6.044839	-3.953732	3.519680
C	-3.712592	-2.126379	2.355084
C	-3.571492	-4.408120	3.444049
C	-3.062482	-3.286125	2.830157
C	-4.907896	-4.783469	3.790484
C	-4.159577	-0.103362	1.343897
C	-6.130376	-2.725940	2.918314
C	-3.103160	-1.005930	1.691761
C	-1.691212	-0.915565	1.406054
C	-0.019951	0.022145	-0.029602
C	-5.127773	-1.881719	2.392147
C	-5.367901	-0.631077	1.776945
H	0.361467	-0.997840	-0.095339
H	-0.608658	0.197399	-2.094590
H	-0.308261	1.752591	-1.308858
O	-0.789972	-1.555431	1.922391
S	-4.100459	1.521235	0.609644
H	-2.838313	-5.158781	3.719146
H	-2.852605	1.419826	0.111552
S	-5.170261	-6.300026	4.557082
H	-6.337057	-0.166328	1.659486
H	-6.982448	-4.390001	3.845721
H	0.584271	0.545016	0.717764
H	-7.139826	-2.328105	2.828899
O	-1.388879	-0.010647	0.394693
H	-1.987562	-3.284203	2.695139
H	1.052680	0.709552	-1.761768

Table A2.20. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of 6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate anion.



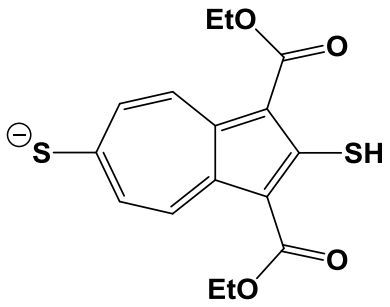
Atom	x	y	z
H	0.128049	0.520660	0.130147
H	9.387768	-0.641488	3.660646
H	9.475861	-3.241281	2.016721
H	10.868497	-2.507429	2.832434
H	0.155831	-1.142135	-0.439781
O	0.827529	-1.066284	2.057623
H	9.370589	-0.720283	1.901535
C	9.781685	-2.625490	2.864388
O	7.686741	-1.494797	2.828032
H	6.510251	-1.464516	5.093131
H	4.024731	-4.514862	7.951628
H	1.399048	-1.957503	3.909784
C	2.503193	-2.539185	5.601316
C	3.381594	-1.430738	3.499158
S	3.276310	-3.391040	8.076296
C	6.888341	-0.389244	2.686404
C	4.825622	-1.326670	3.828828
C	1.911127	-0.819227	1.538241
C	5.454066	-0.750017	2.739611
O	1.973794	-0.411626	0.245705
C	3.213044	-0.907859	2.194361
C	5.448152	-1.679205	5.047131
H	1.574558	-2.939738	5.994284
C	2.395875	-1.968470	4.328533
C	3.603198	-2.675130	6.437515
C	4.510553	-0.493966	1.675292
H	1.638546	1.188654	-1.792966
C	1.038430	0.278495	-1.827300
H	1.604280	-0.471900	-2.381751
H	0.110650	0.489371	-2.367192
C	4.921810	-2.252860	6.183443
H	5.623226	-2.403666	6.997536
C	9.106097	-1.268130	2.808677
S	4.969067	0.102170	0.158265
O	7.352572	0.718388	2.571328
C	0.725508	-0.208791	-0.424397
H	9.517808	-3.157206	3.781394

Table A2.21. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of 6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate anion.



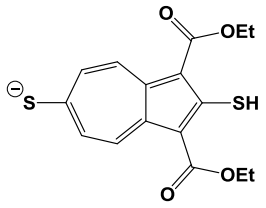
Atom	x	y	z
C	0.338162	0.181570	0.054844
C	0.067273	-0.355339	-1.340324
H	0.831768	-0.016377	-2.042399
H	-0.903833	-0.001274	-1.697700
H	0.062767	-1.447223	-1.345414
O	1.597604	-0.348709	0.484198
C	2.214565	0.272857	1.559329
C	3.487413	-0.381871	1.890837
C	3.975201	-0.581729	3.245681
C	5.212004	-1.332153	3.107728
C	5.506001	-1.530370	1.759021
C	6.589792	-2.258047	1.230819
C	6.965599	-2.492842	-0.081166
C	6.384290	-2.039873	-1.272158
C	5.211301	-1.293590	-1.401145
C	4.340996	-0.826368	-0.425473
C	4.399760	-0.919031	0.974546
H	3.477002	-0.303013	-0.810718
H	4.928640	-1.047980	-2.419293
S	7.202925	-2.512388	-2.824132
H	8.211560	-1.605722	-2.805168
H	7.852542	-3.105786	-0.201713
H	7.243503	-2.695264	1.972952
C	5.962746	-1.886941	4.244955
O	7.329802	-1.780113	4.069749
C	8.151439	-2.301850	5.124238
C	9.554927	-2.500345	4.577910
H	10.217108	-2.855910	5.372390
H	9.959913	-1.567642	4.179387
H	8.146500	-1.591346	5.956908
H	7.725404	-3.236041	5.493087
O	5.500279	-2.405329	5.233090
S	3.288627	-0.037392	4.684191
O	1.698444	1.216002	2.110801
H	-0.438483	-0.135008	0.758423
H	0.366941	1.273344	0.069391
H	9.560514	-3.240903	3.775328

Table A2.22. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of 2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate anion.



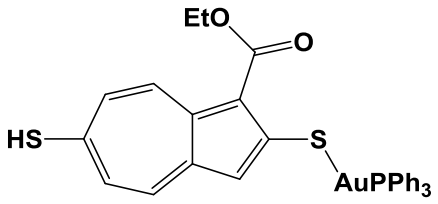
Atom	x	y	z
C	0.226212	0.168969	0.222240
C	-1.073003	-0.265432	0.868102
C	2.563659	-0.231465	0.405640
C	3.657567	-0.751272	1.198793
C	5.026113	-0.441292	0.951473
C	5.823888	-1.032060	1.958738
C	4.949016	-1.741813	2.855973
C	5.342580	-2.444668	4.022300
C	4.623311	-3.183496	4.926726
C	3.230724	-3.497864	4.997588
C	2.293619	-2.985219	4.047599
C	2.456182	-2.170739	2.954330
C	3.610108	-1.577645	2.384074
C	7.269175	-0.887557	1.977185
C	9.335603	-1.491941	3.012113
C	9.778004	-1.983933	4.377996
H	0.258478	-0.109635	-0.832909
H	-1.214769	-1.343970	0.773577
H	-1.910035	0.234964	0.374643
H	-1.093809	-0.000757	1.927378
O	1.311443	-0.463565	0.918804
H	1.537648	-1.945938	2.433495
H	1.274982	-3.304228	4.240646
S	2.670993	-4.509271	6.264739
H	5.200809	-3.622685	5.733056
H	6.401388	-2.394058	4.230647
O	7.908811	-1.631693	2.940898
H	10.859671	-1.860265	4.485507
H	9.529966	-3.037703	4.522182
H	9.289165	-1.409079	5.165707
H	9.793385	-2.076099	2.208140
H	9.609455	-0.448925	2.850556
O	7.913804	-0.181834	1.219939
S	5.693019	0.510427	-0.383961
H	4.476012	0.690380	-0.957919
O	2.663501	0.402697	-0.642529
H	0.352324	1.253667	0.284534

Table A2.23. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of 2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate anion.



Atom	x	y	z
C	0.217706	0.036010	-0.045310
C	-1.101092	-0.569676	0.391684
C	2.542610	-0.048308	0.497092
C	3.598200	-0.610994	1.323188
C	3.518777	-1.472114	2.455643
C	4.826642	-1.711366	2.947191
C	5.751051	-1.009592	2.096474
C	7.161751	-1.027758	2.235085
C	8.146548	-0.421989	1.500695
C	8.079875	0.437401	0.358779
C	6.833245	0.807775	-0.242460
C	5.535814	0.488469	0.071692
C	4.999656	-0.321836	1.103968
C	5.221002	-2.476126	4.119628
C	4.447174	-3.658385	6.044027
C	3.126339	-4.002948	6.706197
H	0.402446	-0.148984	-1.106179
H	-1.123337	-1.646111	0.206605
H	-1.916005	-0.111174	-0.173594
H	-1.282795	-0.389984	1.453798
O	1.273206	-0.559968	0.725893
H	4.791238	0.933570	-0.572817
H	6.951394	1.461832	-1.099776
S	9.540420	1.038724	-0.307077
H	9.160327	-0.617513	1.833152
H	7.513270	-1.630471	3.061421
O	4.150359	-2.932488	4.843409
H	3.305762	-4.581330	7.616772
H	2.504289	-4.599283	6.036598
H	2.573682	-3.100532	6.972181
H	5.018821	-4.557124	5.796170
H	5.076173	-3.043038	6.692040
O	6.359396	-2.715569	4.493255
S	2.061217	-2.174844	3.196378
H	1.222909	-1.710038	2.250017
O	2.670136	0.811634	-0.359191
H	0.227792	1.117126	0.111369

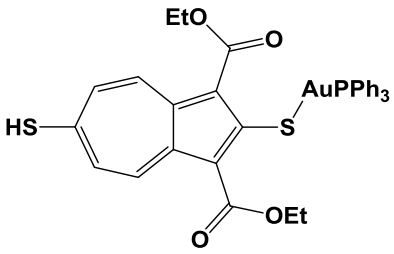
Table A2.24. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of [Ph_3PAu](1-ethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
P	6.830191	4.782352	-5.664266
C	5.207879	5.078457	-6.499602
C	4.943408	6.245945	-7.231983
C	3.702269	6.415398	-7.853820
C	2.722602	5.423920	-7.749012
C	2.981820	4.260807	-7.016066
C	4.217009	4.088779	-6.388060
H	4.410813	3.190527	-5.798230
H	2.215975	3.489348	-6.921715
H	1.753644	5.560186	-8.231261
H	3.500676	7.328140	-8.416534
H	5.700759	7.028106	-7.307993
C	7.617942	6.450283	-5.526800
C	8.582259	6.910560	-6.435144
C	9.146981	8.179975	-6.272184
C	8.750288	8.995382	-5.208935
C	7.790325	8.538154	-4.299452
C	7.231609	7.267857	-4.450553
H	6.501208	6.901761	-3.725399
H	7.485026	9.166269	-3.461348
H	9.194599	9.983569	-5.083219
H	9.902145	8.528705	-6.978565
H	8.900316	6.276682	-7.263912
C	7.849870	3.860679	-6.901771
C	7.582691	3.908856	-8.278701
C	8.392770	3.203599	-9.173657
C	9.472070	2.450552	-8.701474
C	9.737692	2.395709	-7.329234
C	8.926663	3.091629	-6.430160
H	9.117402	3.027111	-5.356422
H	10.570915	1.799399	-6.954517
H	10.100793	1.898513	-9.401635
H	8.175821	3.240122	-10.242589
H	6.735446	4.485932	-8.652458
Au	6.639253	3.731500	-3.616058
S	6.325334	2.621403	-1.588956
C	7.740959	3.008247	-0.624007
C	8.788191	3.888463	-0.977324
H	8.839590	4.444971	-1.910862
C	9.731922	3.933254	0.054242
C	9.261642	3.027381	1.129873
C	8.024573	2.467221	0.682814
C	7.137154	1.510848	1.346691
O	6.063006	1.124107	0.903259

O	7.619234	1.051464	2.558878
C	6.755099	0.101285	3.238719
C	7.433168	-0.285921	4.539865
H	6.805500	-1.009289	5.080828
H	8.410063	-0.752860	4.354745
H	7.580653	0.589529	5.187266
H	5.774125	0.568425	3.409506
H	6.596181	-0.768089	2.584353
C	9.922787	2.792696	2.338285
C	11.129403	3.312748	2.826504
C	12.020123	4.221211	2.241101
C	11.908222	4.847496	0.979723
C	10.903412	4.711747	0.033077
H	11.040673	5.304362	-0.877443
H	12.720743	5.528403	0.710743
S	13.511637	4.700597	3.128357
H	13.275707	3.965184	4.247639
H	11.406745	2.942908	3.816712
H	9.422724	2.092946	3.007840

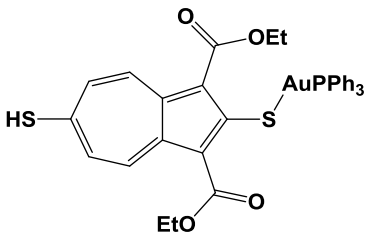
Table A2.25. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of [Ph_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
C	0.34421777046452	0.15909740083369	-0.12945479986260
O	1.17095402252342	-0.75441942628693	0.64663512720340
C	2.04341352229828	-0.16879231755568	1.52909448538658
C	2.86175529313906	-1.15928151722089	2.23705577684054
C	3.19205615923543	-1.14931514121650	3.63399030196180
C	4.00352419195290	-2.30789452964013	3.89871166422590
C	4.21734414464354	-3.00272774643968	2.67750758834812
C	4.98568553692734	-4.16776166351803	2.52062657105349
C	5.25415906404037	-4.92746325840928	1.38475221414150
C	4.82652234982839	-4.72950248092611	0.06027142565608
S	5.33818271235268	-5.88604631266308	-1.21583457958065
H	6.09065664997838	-6.68479639737785	-0.41216709352575
C	4.00455124234336	-3.69418489463110	-0.42062672240155
C	3.41910572099948	-2.63572474648516	0.26900314308602
C	3.47131035639889	-2.29302745954551	1.62956075072258
H	2.81077989763441	-1.97470950017729	-0.34988702807817
H	3.78962161977601	-3.71893131651233	-1.49328697734852
H	5.89095704723106	-5.79870011093049	1.56132920032076
H	5.45953853810682	-4.51786797344646	3.43997666391583
C	4.56878844191784	-2.76866050466896	5.18003358132250
O	3.83028112135237	-2.38278031800075	6.25699350016708
C	4.36355742721275	-2.76427002611089	7.55510318650625
H	4.43156955041697	-3.86175263919671	7.60242025821776
H	5.38474803165894	-2.36564987813961	7.65009394673627

C	3.43101589945339	-2.20309373037420	8.61094296565718
H	3.80107467496097	-2.47412232553118	9.61117468320688
H	2.41611123846961	-2.60844125632361	8.49869070914251
H	3.37499567037547	-1.10825879394184	8.54455730947405
O	5.58084759018665	-3.45735921169607	5.29619457128589
S	2.67919798942337	-0.06180688743404	4.91457813412319
Au	2.30548105447345	2.12298004141677	4.18541911793559
P	2.04157944507599	4.39915649911195	4.04196854920549
C	0.98537795520282	5.06286192052078	5.41103324560662
C	1.29205636030398	6.24674249259505	6.09773192329936
C	0.45068714101953	6.70272430288297	7.11814128348954
C	-0.69746091221304	5.98239768866016	7.45699351721300
C	-1.00312380520223	4.79809049862209	6.77796039775638
C	-0.16336494077420	4.33503656100134	5.76382267489168
H	-0.38767374872223	3.39642540805780	5.25214005249736
H	-1.89196741669164	4.22516186027684	7.04762309444897
H	-1.34973163670957	6.33748085273191	8.25696406970508
H	0.69843304714945	7.62218318273465	7.65144222794006
H	2.19231456190736	6.80986016622951	5.84593166901871
C	3.64941943670909	5.30602501733831	4.19126510445304
C	3.88317153235281	6.53544634154532	3.55626562758039
C	5.11003230880943	7.18626892703216	3.72058435105979
C	6.10849448124881	6.61421273757804	4.51438982099105
C	5.88189425734603	5.38512322751544	5.14203198093516
C	4.65983628689087	4.72913484316092	4.97834482653749
H	4.48915020761483	3.75642494170283	5.44529276573619
H	6.66364626995641	4.92766872105211	5.75080567708114
H	7.06695298408003	7.12198659940613	4.63669245636714
H	5.28587188722569	8.14051829924160	3.22124168396972
H	3.11271963164761	6.98087765539369	2.92471111391314
C	1.26965084988953	5.05530343405557	2.49448688325410
C	0.48975189250529	6.22299939797491	2.48830715370246
C	-0.03598914887618	6.70735752261627	1.28704430361521
C	0.21294801815114	6.02975456214342	0.08939214768145
C	0.97828984877843	4.85927201920357	0.09641741805423
C	1.50146357798883	4.36400307549276	1.29397590759208
H	2.06365802690210	3.42803794526558	1.30161251399911
H	1.16281740082634	4.32086678132251	-0.83472307359233
H	-0.19788345805191	6.40881609018656	-0.84793256333040
H	-0.64337432011577	7.61432980102013	1.28897638648493
H	0.28535455281035	6.74976407457196	3.42180821696359
O	2.08899920525178	1.05191954122974	1.66586667666338
H	-0.18210930459410	0.83257970631343	0.56244073362931
H	0.99763222026192	0.77774527297668	-0.76450784019106
C	-0.61734592524033	-0.68007028583438	-0.94788533705003
H	-1.26904565423970	-0.02243989805974	-1.54189723598001
H	-1.25276782145828	-1.29633639855642	-0.29698782563173
H	-0.08104255479345	-1.34558173416432	-1.63854173540132

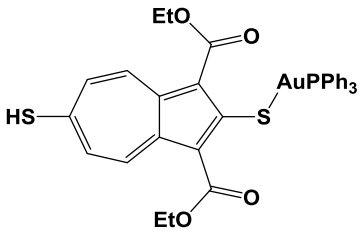
Table A2.26. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of [Ph_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
C	-0.01165078518573	0.16718187124545	0.03761655623348
O	1.03907609633180	-0.68013762227235	0.58014384470005
C	2.26017085153541	-0.57587779728804	-0.00989979359897
C	3.25307011641204	-1.46648492547120	0.62017597013409
C	3.44559768908767	-1.72955303098304	2.00917133253201
C	4.39516125946658	-2.79698579358619	2.13628421515635
C	4.82286949655569	-3.17580829944120	0.83079598469335
C	5.72411011114838	-4.19837851008149	0.50430569736082
C	6.19961086997786	-4.62539783211317	-0.73621655217219
C	5.89163293739595	-4.15405660901226	-2.02301092962496
S	6.68921485779883	-4.89819544418784	-3.45129211515216
H	7.34024597397355	-5.88389910587705	-2.77651784488276
C	4.99981329043358	-3.11793872490636	-2.36175824334664
C	4.22098448890753	-2.32249288079825	-1.52848524837376
C	4.11060739244528	-2.31126795031062	-0.12827755648821
H	3.61294338049543	-1.57066823251600	-2.03742331515008
H	4.89695592700523	-2.90887415852771	-3.43104544865874
H	6.91977741873024	-5.44687948963495	-0.68535511775464
H	6.13050652576203	-4.73760998833115	1.35987256001434
C	4.79122771035294	-3.36345335161969	3.43338014944554
O	6.02329949970911	-3.98856841473389	3.40020749101630
C	6.43846517832611	-4.58605777067067	4.65975386032228
H	6.46438847337028	-3.80207570482811	5.43121897600569
H	5.68610371629834	-5.32669170445535	4.96952849038286
C	7.80223272968934	-5.21390041963308	4.44286812910207
H	8.15680820047467	-5.66144479332300	5.38296183595153
H	8.53748262769729	-4.46259507783935	4.12278145449701
H	7.76079781850358	-6.00753027813637	3.68300008167371
O	4.12909823610628	-3.30084605616703	4.45831027030676
S	2.76689796086990	-0.85892109408744	3.38295388485719
Au	2.75127793508326	1.37968477516882	2.72115960328936
P	2.88077821074054	3.65283923462099	2.33982405457257
C	2.02934990581564	4.62523575497974	3.66407116517924
C	2.54709660779738	5.83014101112913	4.16317230131133
C	1.85358665895198	6.53211515187325	5.15455159222261
C	0.64443835858261	6.03747629570805	5.65188607847377
C	0.12909765702678	4.83277012182724	5.16133751519977
C	0.82025183258930	4.12464189739035	4.17595575739815
H	0.43096100295125	3.17229448309072	3.81036977126155
H	-0.80786742256278	4.43637244899854	5.55499993889347
H	0.10778930823207	6.58543997769195	6.42834352732241
H	2.26384229977975	7.46624310028080	5.54129260528028
H	3.49594397504447	6.21609618059007	3.78801945670183
C	4.62362527299310	4.27333443762390	2.32797093648288

C	5.02623148071596	5.35302732201764	1.52737882154833
C	6.35004330462068	5.80166720632829	1.57243400515260
C	7.27653281098851	5.17443798433559	2.41029040550796
C	6.88047279714957	4.09132746069025	3.20170713106753
C	5.56045921057325	3.63708451265037	3.15860560967142
H	5.25504263361886	2.77648833410834	3.75852734240849
H	7.60361589920089	3.58900968162145	3.84634577874979
H	8.31016329813336	5.52358402353786	2.43980729731781
H	6.65766627439383	6.64042247388739	0.94520922725290
H	4.31062703743897	5.83692143767231	0.86034920109846
C	2.15024660495944	4.25293853420773	0.75195220696989
C	1.45149260997058	5.46768476293196	0.66634578757549
C	0.93701205557713	5.89256086807579	-0.56241994117889
C	1.11518582741510	5.10874333060885	-1.70665864278740
C	1.80293343028915	3.89381927372690	-1.62077995313843
C	2.31591207662390	3.45968099954594	-0.39585386496758
H	2.82478035723621	2.49526274021446	-0.34169960900313
H	1.93118811357267	3.26638353259381	-2.50399563013594
H	0.70966011028691	5.44035555468470	-2.66406570684507
H	0.39237845238403	6.83654502908232	-0.62260697523001
H	1.30346032651725	6.07800773364553	1.55846580023032
O	2.46330928769942	0.12455063405970	-1.00074261447581
H	0.27172105586880	1.21947839951749	0.19307695441615
H	-0.08354736420341	-0.00386313159253	-1.04705810752820
C	-1.29532063502459	-0.18747381546511	0.76175957972623
H	-2.11718468403958	0.44091344669896	0.38845774935151
H	-1.19434849405351	-0.02420046269439	1.84325270285899
H	-1.56312534061384	-1.24000313807769	0.59545650161507

Table A2.27. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of [Ph_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).

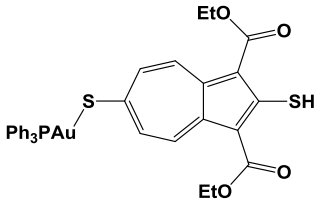


Atom	x	y	z
C	0.43217888207331	0.31095421347271	-0.25314076095580
O	1.17966115645498	-0.66206889004523	0.53071991876868
C	2.07084131429843	-0.14174371628971	1.43578383487518
C	2.81031976939651	-1.18779964105037	2.15057622918274
C	3.12396966870306	-1.19862131538270	3.55073712458887
C	3.87103598086253	-2.39851413563585	3.82177849052324
C	4.04173769949873	-3.11699668815256	2.60965483746847
C	4.69932760431531	-4.34862489239094	2.45383854627543
C	4.90886948933195	-5.13193625553265	1.32153462415081
C	4.52188975893853	-4.89626019801174	-0.00923624778504
S	4.94971988194959	-6.09263468680613	-1.28066637128052
H	5.60006721387307	-6.96626047799221	-0.46572772614461
C	3.80192513829151	-3.79249430651131	-0.49849909238755
C	3.29385635878433	-2.69307462650852	0.18927539727949
C	3.35236649394063	-2.35858991764762	1.55140791003007

H	2.74859855474671	-1.98361677007108	-0.43485144658371
H	3.60186140901260	-3.79456601214795	-1.57418869515613
H	5.45958497748617	-6.05812473591351	1.50633762576508
H	5.12586639761110	-4.75295943351759	3.37218267224700
C	4.32003736125192	-2.79436395781719	5.16852070538937
O	5.48730901632530	-3.53374822525945	5.14306075414451
C	5.96485789275081	-3.96486117607706	6.44798799516798
H	6.10907811220530	-3.07715326090188	7.08143867654875
H	5.19192062717573	-4.58647855973680	6.92526055047741
C	7.25870486999015	-4.72735009341202	6.23405454020352
H	7.65699450409955	-5.05808765838123	7.20419987655676
H	8.01531862454335	-4.09448983719800	5.74965167359582
H	7.09982213079500	-5.61817214343437	5.61020610622675
O	3.76080686775082	-2.51329019636564	6.21622543706798
S	2.65849221018715	-0.11644821518168	4.84805833231251
Au	2.32639878493387	2.08376769564864	4.14886888954906
P	2.10189946472239	4.36732976930303	4.03961278648048
C	1.07222792801781	5.02954261919723	5.42908108204981
C	1.39474660524668	6.21045793309272	6.11398800594060
C	0.57305713358461	6.66556085105329	7.15046056501650
C	-0.57089470083399	5.94715531088552	7.50749616690451
C	-0.89196905315609	4.76584309564019	6.83071256145144
C	-0.07177056890755	4.30362798869779	5.80024302911127
H	-0.30650641077846	3.36638117454312	5.29074752035861
H	-1.77662870432699	4.19381862510058	7.11546009908344
H	-1.20714432003958	6.30115483776065	8.32071059460422
H	0.83336336593508	7.58215165560488	7.68270301568548
H	2.29289084476631	6.77087694415757	5.84888641860074
C	3.72597561449889	5.24535085614331	4.18605071987699
C	3.97934630341362	6.47172544077695	3.55308083895758
C	5.21782996257457	7.10075816652650	3.71568066623581
C	6.20790727040435	6.50976050471558	4.50596180142561
C	5.96145036248964	5.28340171634678	5.13161249511476
C	4.72796546944611	4.64893396197673	4.96936817561806
H	4.54160923370589	3.67856505909942	5.43520408073172
H	6.73623238302731	4.81149271477436	5.73825496386332
H	7.17519389734543	7.00068982608116	4.62748094416549
H	5.40902820249870	8.05309288639827	3.21829460848529
H	3.21473767449766	6.93175966842841	2.92479173012059
C	1.32837709383855	5.05845871096377	2.50787220839995
C	0.55446364556095	6.22979196761333	2.52625440142650
C	0.02746975463105	6.73965374950709	1.33604856047945
C	0.26971856686285	6.08431042407340	0.12484524154659
C	1.02937932744586	4.91012310799959	0.10725426965411
C	1.55329502485232	4.38914109039570	1.29348151982722
H	2.11088511850873	3.45045252769052	1.28125553264398
H	1.20926575520775	4.38935496295225	-0.83476278690547
H	-0.14159662863148	6.48354062274651	-0.80385180976394
H	-0.57530156945119	7.64942399609936	1.35740807458679
H	0.35579137408898	6.73994464244014	3.47006961054659
O	2.19572045647703	1.07140501724114	1.58535670845895

H	-0.06420377214202	1.01145693252478	0.43415503175239
H	1.13948547485526	0.89021290202179	-0.86716119201537
C	-0.56365638934529	-0.45506164663645	-1.10149572783192
H	-1.15574090617448	0.24951749848859	-1.70405701482076
H	-1.25402373854331	-1.03257330218588	-0.47155351666382
H	-0.05672386775200	-1.14929555598809	-1.78606486930573

Table A2.28. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of [Ph_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate).

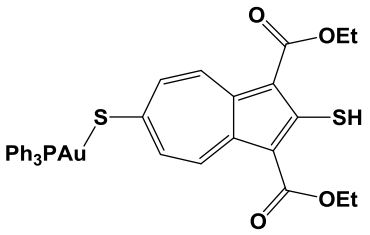


Atom	x	y	z
C	0.35165505776517	-0.11865796190498	-1.68183668753011
C	-0.64809623099006	-1.25812772308861	-1.62290035120010
H	-1.57779249756639	-0.96002912046104	-2.12934095974073
H	-0.89433329409447	-1.51950606301325	-0.58444603487844
H	-0.25814805851984	-2.15442181171289	-2.12477224738694
O	1.55732188426121	-0.55749100885906	-0.99812498080321
C	2.59597306425085	0.35146813462134	-1.01178861872472
C	3.80971918868437	-0.10890531638193	-0.33642637735230
C	4.99789328010029	0.67988478943774	-0.31671679835735
C	6.02243476840579	-0.02943293106620	0.39650094979632
C	5.46233683000471	-1.27904869789988	0.82939978650141
C	6.12281353008144	-2.29070382283754	1.55145997204433
C	5.67352461638844	-3.51746772934314	2.02877751863850
C	4.40303689651338	-4.12685918234496	1.93938859950133
C	3.28423775857285	-3.57006995401812	1.28290982043752
C	3.15117613784459	-2.36201602967153	0.60977146099817
C	4.07217865070778	-1.32302241486052	0.37384229465382
H	2.16258764639416	-2.18505336379938	0.18732956858568
H	2.38083310070094	-4.18661995622816	1.30599962457221
S	4.32440046436684	-5.72700725633132	2.72494753590294
Au	2.10645645697435	-6.43680608442271	2.75631877069775
P	-0.05276198571518	-7.23295174870162	2.89940952561607
C	-1.31033584666188	-5.88251214372509	2.79251836043899
C	-2.51552151760410	-6.03339249498167	2.09018510540917
C	-3.44026477999557	-4.98474240706097	2.05710786561294
C	-3.16771476624439	-3.78597848090839	2.72223186124679
C	-1.96394518240744	-3.63073957558898	3.41827800479161
C	-1.03362895671835	-4.67126808314438	3.44946350845027
H	-0.08555143460609	-4.54266252769791	3.97634573188013
H	-1.74269854316937	-2.69232278323875	3.92897039628108
H	-3.89006405870573	-2.96807916430401	2.69238259785297
H	-4.37430231218785	-5.10567967463786	1.50574489962920
H	-2.73026823730664	-6.96392705136759	1.56219313353643
C	-0.50269511709131	-8.43706936197735	1.57146010015674
C	-1.38068833736431	-9.50787233905719	1.79938861141443
C	-1.70680050435011	-10.37767069057955	0.75401510121600
C	-1.16095107023470	-10.18430826457094	-0.51857141277409

C	-0.27982389513425	-9.12195029262208	-0.74650845131389
C	0.05470860026899	-8.25377756765516	0.29513410998335
H	0.76104210040080	-7.43817307134691	0.12350423388938
H	0.15855814673243	-8.97439349148601	-1.73463658361902
H	-1.41559222843199	-10.86684905109845	-1.33123947158479
H	-2.38577691822655	-11.21223012844125	0.93826213919542
H	-1.80215485438554	-9.66948613854130	2.79254634093712
C	-0.40354659700487	-8.10307364453152	4.49197744270216
C	-1.63559408118539	-7.97953936560915	5.15215193829090
C	-1.85515620195282	-8.66005219738081	6.35398790989933
C	-0.85075225146253	-9.46415702672323	6.90018735738023
C	0.37981895675803	-9.58636838720506	6.24565388323265
C	0.60752386015401	-8.90390000700170	5.04914536531359
H	1.57659651023386	-8.98073381705267	4.55081430226287
H	1.17120296746329	-10.20320844983634	6.67452290674306
H	-1.02214242655780	-9.98837119599633	7.84156821793225
H	-2.81264202739206	-8.55471988067034	6.86726806880960
H	-2.41967061972893	-7.34430119714486	4.73667059281328
H	6.42494627651164	-4.09859109419342	2.57123557812701
H	7.16429061601765	-2.07451786482899	1.78140214245581
C	7.36901902820849	0.49537147514305	0.60473050523961
O	8.20250368496320	-0.33109803863852	1.31329858715633
C	9.54636845281175	0.18176669918940	1.54472376982851
C	10.31387332878117	-0.88143007659573	2.30737581318904
H	11.33479294576995	-0.52462709042386	2.50608046594689
H	10.38442351245959	-1.81298951928865	1.72907841248316
H	9.83706313555914	-1.10292047660392	3.27189879855392
H	10.01089581829842	0.41146742003513	0.57491012927866
H	9.47293971816548	1.12286101992279	2.10912349340166
O	7.78486864100683	1.58997665232915	0.20340067093187
S	5.12111401359238	2.26023963104333	-1.06469432530106
H	6.43982254179066	2.37874465050418	-0.66840091085969
O	2.47979714709931	1.44174470577844	-1.56087824924179
H	-0.02858487136537	0.78838894629742	-1.18863097715709
H	0.60724782929774	0.15184273640172	-2.71674075401516

Table A2.29. Cartesian coordinates (Å) for the optimized structure of a higher energy ester group orientation of [Ph_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate).

Atom	x	y	z
C	-0.17337736301213	-0.06499841280705	0.00155332775937
C	-0.03930053803669	1.41328122133841	-0.30911351930684
H	-1.03730970079831	1.84969764891410	-0.46167938973999
H	0.55056080056193	1.57267203456309	-1.22198170643069
H	0.44845610115886	1.94885821336722	0.51677252823039
O	1.16593175654065	-0.59697683099732	0.18786904196416
C	1.24292781940238	-1.92923530237613	0.49829991500107
C	2.62305755349027	-2.37819381105854	0.69515460999871

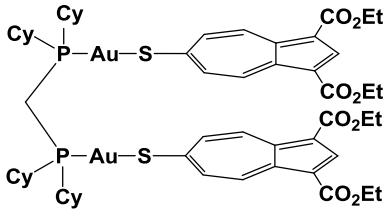


C	3.81474546130739	-1.59075748942012	0.71448504964830
C	4.93873520385507	-2.44827012355646	0.96841024394485
C	4.43496422425517	-3.78911496216520	1.10494910278593
C	5.20040484842564	-4.94190641323017	1.36793183480605
C	4.81192928076608	-6.26582180295246	1.54918182909266
C	3.53037813761774	-6.85945505673069	1.50020077957480
C	2.33239192364838	-6.18006295364663	1.18351482109897
C	2.10391421099917	-4.83157431203595	0.94981473527521
C	2.99170366255636	-3.74027767386119	0.93100054781838
H	1.06507274363581	-4.55861445735910	0.75177086497960
H	1.44497960574160	-6.81597250134584	1.12039243892333
S	3.52620644479422	-8.61317300233187	1.83159986237361
Au	1.30786641023501	-9.19530942153803	2.26524372046420
P	-0.87557533068929	-9.76740048714201	2.73804585423274
C	-2.06016577786049	-8.50962118159535	2.08206854044057
C	-3.25126699856818	-8.86595736881842	1.43256092395119
C	-4.10540708757365	-7.87023381222688	0.94662023477675
C	-3.77575774014359	-6.52133303812328	1.10390251314714
C	-2.58655803350474	-6.16255307082297	1.74890979925469
C	-1.72947068817714	-7.15185843301993	2.23419543184737
H	-0.79587928908181	-6.86816538738857	2.72466288278243
H	-2.31448615238631	-5.11153446146218	1.85897749821330
H	-4.43946976971999	-5.74732207221445	0.71551728826915
H	-5.02811366773552	-8.15407451157741	0.43768426082490
H	-3.50841156852302	-9.91740709146486	1.29576048432151
C	-1.40110833354759	-11.38299365886783	2.01192931505896
C	-2.31561490363673	-12.23005714809418	2.65594115271796
C	-2.69188348891528	-13.43569153823934	2.05610759635048
C	-2.16022768206299	-13.80051793217043	0.81583392564428
C	-1.24445936291163	-12.96049900055388	0.17372574914149
C	-0.85975145627777	-11.75820592401978	0.77082134399889
H	-0.12898630514882	-11.11055601000337	0.28024913176899
H	-0.81944863902205	-13.24581054384130	-0.78954041174276
H	-2.45351018064004	-14.74420841375602	0.35327669287590
H	-3.39927498830265	-14.09385079392858	2.56396600519959
H	-2.72576360347789	-11.95436883396479	3.62826192758879
C	-1.24837090354660	-9.89318604439983	4.54380477120127
C	-2.49699103393996	-9.52789763187369	5.07057570710336
C	-2.74159693423544	-9.65771808478078	6.44119660981255
C	-1.74435520013106	-10.14845622802926	7.28940292137273
C	-0.49615883312726	-10.50557036602134	6.76789643574817
C	-0.24497650744850	-10.37456136970511	5.40047167422624
H	0.73645300713892	-10.63178410545288	4.99616532807732
H	0.28934898661020	-10.87537975674141	7.42891774167966
H	-1.93664983430170	-10.24394777413777	8.35957475632964
H	-3.71220136675988	-9.36689516319169	6.84655955968663
H	-3.27273299230443	-9.12994555018858	4.41422443342792
H	5.62913283723306	-6.95448723552999	1.78147056490576
H	6.27124884741823	-4.75516193870421	1.46148963424682
C	6.36393859443021	-2.12833111055328	1.08857240590778
O	6.66329368488590	-0.78524968568871	0.93027778693456

C	8.07416048229696	-0.44041810378926	1.03840005153006
C	8.19752751625287	1.05594140644582	0.82364576896966
H	9.25432579442930	1.35109125399832	0.89666869727714
H	7.63551434922661	1.61691140423468	1.58318882228395
H	7.83173944111987	1.34794386399957	-0.17074427461994
H	8.43725055347436	-0.74677486569160	2.03019961993334
H	8.63605982159037	-1.01393503234220	0.28710092460874
O	7.26593718762618	-2.93146983117124	1.30928197708023
S	3.80495893718913	0.15553598547853	0.46511720456230
H	5.15344660941526	0.27475461173477	0.64125652415109
O	0.23147250547169	-2.62490385165355	0.59042064755501
H	-0.66309697278473	-0.61632799454518	-0.81564031111403
H	-0.75675418646705	-0.24345721917436	0.91744767819563

Table A2.30. Cartesian coordinates (Å) for the optimized structure of [Au_2(dcpm)(1,3-diethoxycarbonyl-6-mercaptoazulene)$_2$].

Atom	x	y	z
P	0.436246	-0.204870	-0.461468
Au	1.063261	-2.398580	-0.852155
Au	3.013726	-1.126960	-3.066731
S	2.624099	-2.490575	-4.931375
C	2.639347	-1.452793	-6.378308
C	2.782898	-0.049866	-6.263637
C	2.827274	0.931711	-7.245216
H	2.953709	1.957246	-6.888407
C	2.735710	0.821005	-8.640424
C	2.796513	1.904626	-9.576901
C	2.664936	1.364969	-10.871316
C	2.520791	-0.034046	-10.794821
C	2.559883	-0.409176	-9.412004
C	2.451708	-1.715059	-8.903493
C	2.483912	-2.171363	-7.590417
H	2.381069	-3.253469	-7.472615
H	2.324405	-2.483464	-9.669912
C	2.363427	-0.941077	-11.934423
O	2.375257	-0.259424	-13.127556
C	2.241099	-1.084016	-14.316112
H	3.060205	-1.819027	-14.334307
H	1.295965	-1.644102	-14.257529
C	2.280497	-0.161154	-15.518183
H	2.183403	-0.751707	-16.440560
H	3.229233	0.390725	-15.562911
H	1.456573	0.565105	-15.487767
O	2.235681	-2.161149	-11.880375
H	2.674523	1.940476	-11.791922
C	2.969988	3.319648	-9.250461
O	2.979594	4.102156	-10.380301



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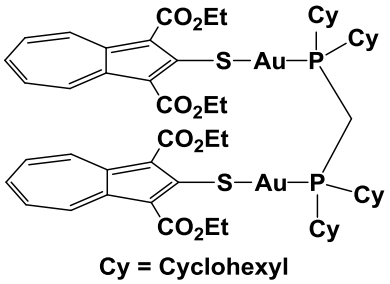
C	3.156936	5.525007	-10.153561
H	2.364615	5.882090	-9.478671
H	4.120921	5.688565	-9.647800
C	3.103320	6.212014	-11.504762
H	3.239044	7.295418	-11.373840
H	2.134913	6.043488	-11.995940
H	3.897772	5.843219	-12.167590
O	3.097041	3.800453	-8.125609
H	2.883770	0.311358	-5.235954
P	3.447525	0.251879	-1.262340
C	1.878417	0.996989	-0.551841
H	1.583142	1.844490	-1.184691
H	2.084278	1.389455	0.454346
C	4.206133	-0.631690	0.219062
H	3.327863	-1.158982	0.638226
C	5.219368	-1.717869	-0.197433
H	6.086177	-1.255959	-0.696058
H	4.754884	-2.395535	-0.929572
C	5.701555	-2.508492	1.029532
H	4.854997	-3.081108	1.444661
H	6.452400	-3.248929	0.715134
C	6.277114	-1.585458	2.111338
H	7.194127	-1.101284	1.731904
H	6.575622	-2.171555	2.993569
C	5.265274	-0.504681	2.516785
H	4.397667	-0.981087	3.003549
H	5.706375	0.180416	3.257788
C	4.780924	0.302527	1.297970
H	5.631735	0.868526	0.883776
H	4.033892	1.047280	1.619106
C	4.498480	1.762778	-1.669160
H	4.571041	2.347105	-0.734439
C	3.830386	2.634217	-2.752769
H	3.671873	2.021337	-3.655846
H	2.837915	2.980535	-2.425752
C	4.697260	3.853024	-3.112107
H	4.765766	4.522423	-2.236625
H	4.202119	4.425400	-3.911145
C	6.107355	3.435408	-3.547695
H	6.719461	4.326258	-3.754749
H	6.044161	2.871794	-4.493641
C	6.776816	2.565063	-2.477348
H	6.953613	3.169069	-1.570088
H	7.764053	2.221428	-2.821310
C	5.915639	1.343627	-2.113312
H	5.831571	0.675374	-2.987259
H	6.414206	0.766519	-1.321289
S	1.701178	-4.625618	-1.184971
C	1.693338	-5.437211	0.402106
C	1.082117	-4.830016	1.523988
C	0.997589	-5.262538	2.842050

H	0.479423	-4.592106	3.532035
C	1.476907	-6.437454	3.440510
C	1.351827	-6.789793	4.824661
C	1.941476	-8.056457	5.003837
C	2.442686	-8.530059	3.776267
C	2.171222	-7.540941	2.775212
C	2.513721	-7.623332	1.415073
C	2.313718	-6.711128	0.385066
H	2.706761	-7.017087	-0.587795
H	3.028686	-8.546799	1.138780
C	3.125880	-9.809580	3.568920
O	3.214776	-10.528863	4.736234
C	3.882873	-11.814982	4.625620
H	4.909205	-11.653566	4.263623
H	3.359473	-12.425410	3.875131
C	3.859989	-12.459193	5.999083
H	4.359244	-13.437554	5.956169
H	2.829486	-12.614205	6.345529
H	4.385341	-11.837363	6.736340
O	3.579015	-10.228176	2.507438
H	2.001893	-8.588123	5.948678
C	0.734466	-5.977446	5.872255
O	0.762769	-6.618926	7.088939
C	0.185335	-5.895417	8.209445
H	-0.171362	-6.685374	8.883048
H	-0.668840	-5.306200	7.850211
C	1.215104	-5.006807	8.891958
H	0.770246	-4.539778	9.783266
H	1.549557	-4.208154	8.217354
H	2.088510	-5.591260	9.211463
O	0.237980	-4.861084	5.728342
H	0.608122	-3.866834	1.316193
C	-0.293935	0.048566	1.256689
H	-1.165819	-0.628251	1.254131
C	-0.782008	1.481458	1.538706
H	0.070245	2.181638	1.477480
H	-1.510639	1.802358	0.779102
C	-1.415271	1.586303	2.939028
H	-2.338846	0.983976	2.961386
H	-1.716117	2.628334	3.127532
C	-0.460367	1.093074	4.034353
H	0.409819	1.770113	4.093020
H	-0.956029	1.135362	5.016235
C	0.023770	-0.334195	3.746750
H	-0.828875	-1.031776	3.802427
H	0.741632	-0.662878	4.512645
C	0.670956	-0.439069	2.355140
H	1.586845	0.176961	2.343649
H	0.981905	-1.475322	2.152960
C	-0.837341	0.479394	-1.663147
H	-0.990733	1.534630	-1.372232

C	-0.331092	0.433583	-3.117149
H	0.602530	1.006689	-3.224967
H	-0.084253	-0.607393	-3.383102
C	-1.390073	0.974347	-4.092239
H	-1.005044	0.897366	-5.120356
H	-1.556983	2.048258	-3.897474
C	-2.717246	0.216824	-3.956031
H	-3.471166	0.644647	-4.634154
H	-2.571045	-0.831063	-4.268320
C	-3.224819	0.250833	-2.508730
H	-4.147351	-0.340763	-2.408343
H	-3.485745	1.288133	-2.235536
C	-2.171557	-0.281656	-1.521145
H	-2.559609	-0.204416	-0.493566
H	-1.991897	-1.352927	-1.713739

Table A2.31. Cartesian coordinates (Å) for the optimized structure of [Au_2(dcpm)(1,3-diethoxycarbonyl-2-mercaptoazulene)$_2$].

Atom	x	y	z
Au	6.998113	2.799124	4.049195
Au	7.217608	5.956214	3.534434
S	9.219763	2.697725	4.783692
S	8.039622	6.510201	5.658931
P	4.864541	2.978868	3.173851
P	6.299098	5.284810	1.521746
O	12.152216	2.720487	4.455720
O	13.034384	1.585685	2.687842
O	7.670590	0.264397	6.283755
O	6.835635	-1.133437	4.688885
O	7.815553	6.902028	8.603590
O	5.888761	7.830522	9.391373
O	9.075093	8.973106	3.746735
O	7.197838	9.762347	2.730001
C	11.027148	0.788935	3.743454
C	9.757973	1.078212	4.342119
C	9.001672	-0.134212	4.390358
C	9.326745	-2.495701	3.604276
H	8.327629	-2.708394	3.990405
C	9.992219	-3.566357	3.004186
H	9.444559	-4.512692	3.001444
C	11.255769	-3.598261	2.401641
H	11.560192	-4.563526	1.988381
C	12.180915	-2.559027	2.265055
H	13.113588	-2.821898	1.758957
C	12.093317	-1.230038	2.692049
H	12.952206	-0.593504	2.470611
C	9.745320	-1.165560	3.760176



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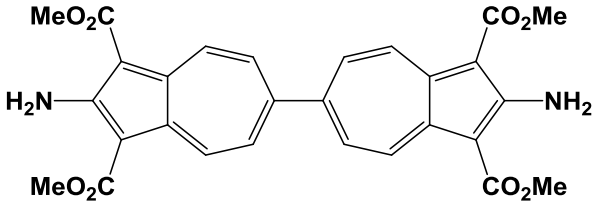
C	13.194931	3.727112	4.330237
H	12.717975	4.648978	4.686355
H	13.462268	3.831867	3.270419
C	14.409752	3.368044	5.171083
H	15.144117	4.187100	5.129893
H	14.890727	2.456343	4.793736
H	14.127131	3.213131	6.221207
C	7.726121	-0.380262	5.084426
C	6.463918	0.087521	7.075569
H	5.608551	-0.047790	6.400619
H	6.359006	1.036063	7.617778
C	6.598524	-1.089009	8.029648
H	5.711277	-1.144707	8.678660
H	7.484539	-0.975251	8.668689
H	6.678662	-2.033964	7.476858
C	6.732673	8.471078	7.234751
C	7.332722	8.091506	5.990783
C	7.143011	9.158489	5.060932
C	5.957095	11.367542	5.062398
H	6.260321	11.474828	4.018161
C	5.201525	12.415322	5.591534
H	5.005490	13.242892	4.904473
C	4.658262	12.553703	6.875244
H	4.095388	13.473819	7.055070
C	4.747032	11.674478	7.958547
H	4.245353	12.001597	8.872899
C	5.393118	10.436449	8.048725
H	5.321335	9.922544	9.009621
C	6.364377	10.172022	5.673127
C	6.106526	9.737741	7.066598
C	6.728909	7.720602	8.500599
C	7.896462	6.067243	9.793106
H	7.494206	6.628233	10.647529
H	8.973382	5.908819	9.929635
C	7.162613	4.748990	9.600453
H	7.326750	4.104968	10.478056
H	7.534248	4.224098	8.710447
H	6.082646	4.915757	9.494615
C	7.756372	9.308406	3.728106
C	9.790342	9.078153	2.486504
H	9.594069	10.065339	2.043573
H	9.394901	8.313910	1.798963
C	11.261627	8.860470	2.780844
H	11.838150	8.917120	1.846658
H	11.429096	7.875034	3.234028
H	11.641399	9.627723	3.468718
C	4.767465	4.228468	1.772546
H	4.533916	3.698309	0.837531
H	3.932178	4.908927	1.980998

C	4.197836	1.403921	2.388321
H	3.274750	1.700005	1.856732
C	5.201464	0.836386	1.365430
H	5.431753	1.581794	0.588219
H	6.147756	0.612948	1.886279
C	4.663594	-0.446711	0.709488
H	3.771369	-0.203349	0.105131
H	5.417734	-0.842342	0.011178
C	4.300000	-1.503400	1.761212
H	3.877826	-2.395615	1.273300
H	5.214258	-1.823849	2.286074
C	3.308089	-0.939457	2.786657
H	3.097243	-1.687025	3.565983
H	2.346112	-0.718710	2.290057
C	3.848373	0.341012	3.447838
H	4.755282	0.090340	4.021930
H	3.103863	0.730325	4.159749
C	3.554447	3.528420	4.409535
H	3.573304	2.711661	5.154062
C	2.130670	3.630560	3.832789
H	2.102600	4.402727	3.043385
H	1.828968	2.683844	3.360094
C	1.117602	4.009600	4.929131
H	0.116416	4.113938	4.482494
H	1.051315	3.183738	5.658472
C	1.522655	5.298840	5.656399
H	0.806545	5.520843	6.462306
H	1.472313	6.147351	4.951151
C	2.945404	5.194203	6.221700
H	2.969506	4.425610	7.014039
H	3.244542	6.140285	6.696189
C	3.965106	4.826046	5.131585
H	4.031200	5.653479	4.404010
H	4.971015	4.720902	5.564557
C	5.639430	6.647026	0.398389
H	5.122282	6.125007	-0.427877
C	4.623003	7.532765	1.148808
H	3.795074	6.931532	1.554992
H	5.130659	8.007448	2.004556
C	4.052161	8.624184	0.226991
H	3.353573	9.253081	0.800385
H	3.463593	8.151915	-0.580207
C	5.165922	9.483850	-0.383010
H	4.738227	10.226362	-1.075463
H	5.671064	10.041869	0.421489
C	6.195551	8.610928	-1.110910
H	7.021788	9.229701	-1.493023
H	5.724677	8.136598	-1.990670
C	6.765788	7.519572	-0.187677
H	7.310874	7.998168	0.641917
H	7.487306	6.904295	-0.744949

C	7.424999	4.151698	0.521818
H	7.354757	3.208773	1.096849
C	8.901586	4.590144	0.572179
H	9.020824	5.568751	0.078292
H	9.210535	4.719298	1.620455
C	9.800281	3.555400	-0.124481
H	10.843086	3.906030	-0.111295
H	9.781629	2.616183	0.452393
C	9.344005	3.282602	-1.564291
H	9.473263	4.196665	-2.171032
H	9.977543	2.509004	-2.024985
C	7.871234	2.852696	-1.608547
H	7.761133	1.878953	-1.101910
H	7.540853	2.706676	-2.648940
C	6.959297	3.885815	-0.920806
H	5.915720	3.530124	-0.943192
H	6.983775	4.824842	-1.497957

Appendix 3. Supplementary Information for Chapter 3

Table A3.1. Cartesian coordinates (Å) for the optimized structure of 2,2'-diamino-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl (III.1a').

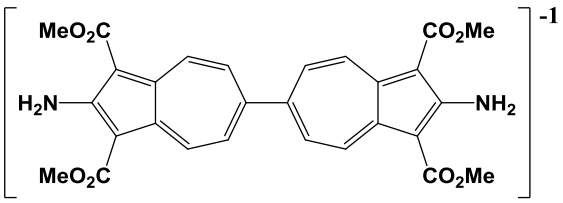


Atom	x	y	z
C	-0.118512	0.174223	-0.035314
O	-0.769903	0.118775	1.246163
C	-1.743562	-0.844011	1.378062
C	-2.363518	-0.843439	2.692170
C	-2.070216	0.031473	3.786250
N	-1.156323	1.009985	3.778206
H	-1.032214	1.564899	4.608757
H	-0.616232	1.162602	2.942693
C	-2.914074	-0.310351	4.890449
C	-3.734694	-1.397329	4.492379
C	-4.707059	-2.019801	5.279396
H	-4.820488	-1.596907	6.268821
C	-5.546683	-3.085218	4.987619
H	-6.226115	-3.342680	5.792224
C	-5.676324	-3.861320	3.826990
C	-4.932860	-3.679190	2.652340
H	-5.144019	-4.386927	1.858750
C	-3.943892	-2.758050	2.336827
H	-3.527588	-2.846513	1.342014
C	-3.385677	-1.735385	3.108233
C	-6.682282	-4.969547	3.846824
C	-6.704059	-5.800693	4.975877

C	-7.510125	-6.885431	5.289795
C	-8.545156	-7.479296	4.562706
C	-9.318539	-8.594233	4.977828
C	-10.253123	-8.893897	3.936323
N	-11.153585	-9.884498	3.959780
H	-11.198838	-10.480581	4.769657
H	-11.764596	-10.003378	3.168906
C	-10.066257	-7.962285	2.865600
C	-9.018525	-7.078827	3.233231
C	-8.539244	-6.013169	2.467280
C	-7.529898	-5.099681	2.737363
H	-7.394693	-4.352367	1.963974
H	-9.044482	-5.879916	1.519630
C	-10.800838	-7.905871	1.613162
O	-10.627497	-7.115885	0.705814
O	-11.771692	-8.875796	1.519720
C	-12.533003	-8.880325	0.299129
H	-13.048685	-7.930489	0.164801
H	-13.249268	-9.690658	0.407219
H	-11.883163	-9.057515	-0.556856
C	-9.166117	-9.284270	6.246996
O	-8.372390	-9.014661	7.127001
O	-10.042395	-10.334326	6.393951
C	-9.943433	-11.058138	7.633235
H	-10.153105	-10.402692	8.477493
H	-8.947483	-11.482978	7.750799
H	-10.689042	-11.846206	7.569225
H	-7.306736	-7.353885	6.243601
H	-5.955211	-5.577033	5.727359
C	-2.945121	0.318751	6.199811
O	-3.664057	0.016746	7.132052
O	-2.042106	1.349590	6.319241
C	-2.018564	2.011550	7.596355
H	-1.750280	1.311003	8.386077
H	-2.991419	2.446459	7.821093
H	-1.264775	2.789281	7.505995
O	-2.008487	-1.585202	0.451950
H	0.372230	-0.772276	-0.257580
H	0.613681	0.973356	0.046098
H	-0.838634	0.395534	-0.821934

Table A3.2. Cartesian coordinates (Å) for the optimized structure of [2,2'-diamino-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1a'$^{-1}$).

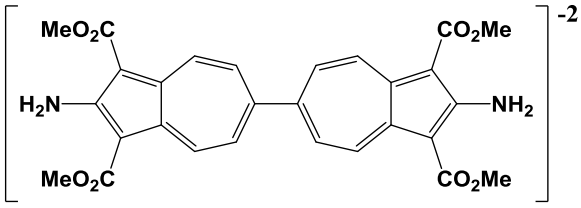
Atom	x	y	z
C	-0.475475	0.553452	-0.170898
O	-0.993373	0.403640	1.152496
C	-1.952850	-0.598212	1.306711



C	-2.438425	-0.711061	2.656767
C	-2.036884	0.066266	3.784759
N	-1.115261	1.057743	3.773609
H	-0.916297	1.538377	4.632786
H	-0.668404	1.288642	2.904257
C	-2.768492	-0.378236	4.927014
C	-3.634036	-1.446112	4.502311
C	-4.535427	-2.156155	5.334688
H	-4.553534	-1.814203	6.360828
C	-5.395737	-3.188369	5.046421
H	-5.995045	-3.491394	5.895971
C	-5.680849	-3.882923	3.833763
C	-5.035239	-3.552525	2.605878
H	-5.301655	-4.183369	1.766938
C	-4.082675	-2.612461	2.292194
H	-3.757386	-2.612780	1.260449
C	-3.432199	-1.649998	3.105024
C	-6.661224	-4.962545	3.852153
C	-6.836514	-5.715169	5.050843
C	-7.665575	-6.765408	5.364218
C	-8.635132	-7.441634	4.581619
C	-9.455788	-8.535389	5.029318
C	-10.285760	-8.929322	3.936814
N	-11.197725	-9.929562	3.958409
H	-11.330089	-10.440971	4.812678
H	-11.734128	-10.108367	3.128379
C	-9.988992	-8.095557	2.816478
C	-8.961521	-7.172316	3.219269
C	-8.390071	-6.166259	2.399999
C	-7.415227	-5.236239	2.672807
H	-7.226814	-4.563484	1.845547
H	-8.806387	-6.118157	1.402545
C	-10.592987	-8.147348	1.511236
O	-10.347831	-7.448602	0.541790
O	-11.571496	-9.136285	1.400345
C	-12.202001	-9.229855	0.121423
H	-12.702809	-8.296749	-0.138973
H	-12.929170	-10.035220	0.210784
H	-11.475860	-9.463260	-0.658156
C	-9.427479	-9.106833	6.349675
O	-8.724606	-8.783373	7.292766
O	-10.334696	-10.154888	6.512101
C	-10.344304	-10.757368	7.807805
H	-10.615056	-10.032067	8.576058
H	-9.367519	-11.175279	8.053834
H	-11.090853	-11.548189	7.758376
H	-7.555498	-7.155503	6.367184
H	-6.164542	-5.449200	5.857446
C	-2.675454	0.129602	6.270401
O	-3.293946	-0.236411	7.256151
O	-1.750900	1.167161	6.399869

C	-1.623850	1.710417	7.715477
H	-1.299856	0.948429	8.425403
H	-2.570379	2.127577	8.061062
H	-0.872707	2.494723	7.638190
O	-2.278164	-1.258561	0.333918
H	0.013938	-0.361300	-0.507087
H	0.245793	1.367038	-0.113564
H	-1.268524	0.802504	-0.876944

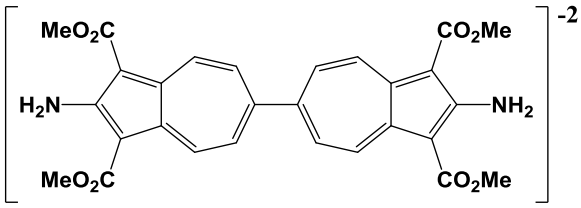
Table A3.3. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [2,2'-diamino-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-2}$ (III.1a'$^{-2}$).



Atom	x	y	z
C	-0.742148	0.873902	-0.222931
O	-1.152257	0.645283	1.117370
C	-2.120266	-0.381203	1.279266
C	-2.494110	-0.592071	2.639322
C	-1.999372	0.102777	3.782033
N	-1.070998	1.104564	3.767804
H	-0.804739	1.519013	4.641648
H	-0.696074	1.393641	2.883424
C	-2.636834	-0.426523	4.942448
C	-3.548433	-1.476298	4.497977
C	-4.399126	-2.257541	5.359634
H	-4.335027	-1.981066	6.404026
C	-5.275501	-3.261748	5.080549
H	-5.799668	-3.607173	5.961748
C	-5.692145	-3.899693	3.840948
C	-5.118221	-3.444388	2.583965
H	-5.439817	-4.002036	1.714371
C	-4.194233	-2.492557	2.275790
H	-3.946310	-2.416507	1.225033
C	-3.464085	-1.574639	3.113228
C	-6.646720	-4.948393	3.858999
C	-6.948202	-5.648635	5.098266
C	-7.793932	-6.670683	5.405729
C	-8.717763	-7.414636	4.587262
C	-9.581574	-8.492466	5.059787
C	-10.322714	-8.966533	3.937615
N	-11.242365	-9.976282	3.956918
H	-11.439447	-10.424176	4.832617
H	-11.704078	-10.215791	3.099206
C	-9.938797	-8.209887	2.791439
C	-8.931738	-7.245418	3.223461
C	-8.285399	-6.280284	2.370421
C	-7.337007	-5.340627	2.639689
H	-7.099119	-4.736740	1.774187
H	-8.631562	-6.302504	1.345162

C	-10.439587	-8.351537	1.463511
O	-10.155563	-7.720101	0.453430
O	-11.406730	-9.383642	1.336289
C	-11.930502	-9.552931	0.027146
H	-12.428560	-8.647629	-0.327053
H	-12.650006	-10.370107	0.097753
H	-11.146450	-9.809651	-0.688992
C	-9.657119	-8.970086	6.401510
O	-9.038455	-8.604745	7.393164
O	-10.597009	-10.021383	6.570121
C	-10.693840	-10.529387	7.892739
H	-11.009117	-9.756816	8.597957
H	-9.740111	-10.934390	8.238419
H	-11.442262	-11.322201	7.853016
H	-7.761559	-6.998734	6.436582
H	-6.346810	-5.343508	5.944404
C	-2.435075	-0.017451	6.293731
O	-2.953778	-0.439333	7.319678
O	-1.491351	1.035672	6.425203
C	-1.279092	1.485248	7.755556
H	-0.903472	0.683730	8.395830
H	-2.199110	1.871680	8.200194
H	-0.537308	2.282291	7.685922
O	-2.509944	-0.951437	0.267952
H	-0.281840	-0.015426	-0.659457
H	-0.013400	1.684618	-0.177156
H	-1.583115	1.165676	-0.856251

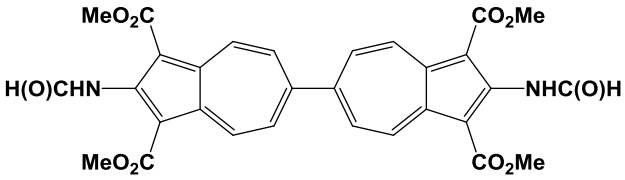
Table A3.3. Cartesian coordinates (Å) for the triplet state (T) optimized structure of [2,2'-diamino-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-2}$ (III.1a'$^{-2}$).



Atom	x	y	z
C	-0.471065	0.650393	-0.156695
O	-0.973835	0.498539	1.160556
C	-1.911762	-0.566662	1.323599
C	-2.384772	-0.713867	2.654630
C	-2.000355	0.051851	3.793911
N	-1.043656	1.021167	3.793931
H	-0.971924	1.590398	4.620056
H	-0.721372	1.343111	2.897194
C	-2.725973	-0.377861	4.943148
C	-3.605633	-1.473740	4.531923
C	-4.468143	-2.178775	5.338890
H	-4.481887	-1.855292	6.372773
C	-5.354304	-3.249474	5.051854
H	-5.957177	-3.543345	5.901059
C	-5.633707	-3.919723	3.834636
C	-5.008044	-3.592840	2.606076

H	-5.254618	-4.229891	1.766773
C	-4.026253	-2.614790	2.296839
H	-3.715300	-2.609753	1.258997
C	-3.393044	-1.683474	3.086821
C	-6.624749	-5.012244	3.849285
C	-6.814815	-5.766012	5.049535
C	-7.637667	-6.819793	5.359365
C	-8.609337	-7.504403	4.556059
C	-9.444611	-8.606286	5.009652
C	-10.273962	-8.994973	3.918688
N	-11.156644	-10.050660	3.917731
H	-11.436002	-10.378236	4.827328
H	-11.833594	-10.043738	3.173259
C	-9.975992	-8.158336	2.804631
C	-8.930137	-7.233792	3.216335
C	-8.352022	-6.216614	2.385901
C	-7.374710	-5.293802	2.664165
H	-7.166815	-4.625444	1.837284
H	-8.762636	-6.171163	1.386264
C	-10.601271	-8.182931	1.518047
O	-10.354514	-7.510715	0.526757
O	-11.653177	-9.123107	1.427411
C	-12.290353	-9.190136	0.158463
H	-12.743929	-8.234620	-0.113467
H	-13.061153	-9.955687	0.253731
H	-11.585757	-9.467781	-0.628385
C	-9.440677	-9.160637	6.328558
O	-8.726452	-8.881231	7.281049
O	-10.420179	-10.162779	6.515304
C	-10.435795	-10.752449	7.808602
H	-10.658578	-10.014938	8.582812
H	-9.476726	-11.216336	8.047925
H	-11.219620	-11.510088	7.779362
H	-7.536307	-7.208390	6.363520
H	-6.155462	-5.482803	5.861330
C	-2.652464	0.160787	6.255146
O	-3.260579	-0.180399	7.266419
O	-1.741692	1.254852	6.377743
C	-1.645604	1.804568	7.681359
H	-1.300660	1.063740	8.407121
H	-2.606241	2.193643	8.027866
H	-0.919984	2.616876	7.610744
O	-2.204284	-1.215937	0.322767
H	0.054842	-0.246259	-0.493975
H	0.221995	1.492809	-0.116840
H	-1.269807	0.860572	-0.872214

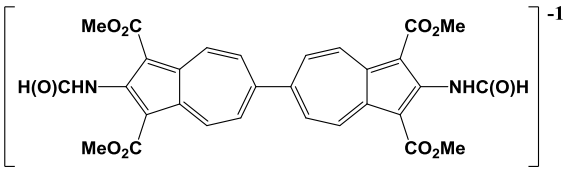
Table A3.4. Cartesian coordinates (Å) for the optimized structure of 2,2'-bisformamido-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl (III.1b').



Atom	x	y	z
C	-0.031534	0.381932	-0.058356
O	-1.442697	0.519614	0.196560
C	-2.278146	0.010738	-0.766942
C	-3.691282	0.193068	-0.450536
C	-4.263579	0.935820	0.624332
N	-3.509201	1.675796	1.522006
C	-3.823822	2.903677	2.065732
H	-2.976232	3.294090	2.654108
O	-4.857925	3.511485	1.931111
H	-2.525511	1.434339	1.528921
C	-5.667714	0.833271	0.580564
C	-6.010614	0.074389	-0.564887
C	-7.309679	-0.220395	-0.982595
H	-8.088951	0.222390	-0.374471
C	-7.750162	-0.956876	-2.072271
H	-8.827988	-0.993036	-2.178903
C	-7.026356	-1.630028	-3.068288
C	-5.630451	-1.698779	-3.156429
H	-5.248042	-2.295234	-3.976509
C	-4.643426	-1.148418	-2.346106
H	-3.625673	-1.366229	-2.642073
C	-4.761248	-0.351547	-1.209130
C	-7.814564	-2.338357	-4.129228
C	-8.861858	-3.169606	-3.704014
C	-9.749835	-3.943490	-4.437334
C	-9.850659	-4.128615	-5.817600
C	-10.811946	-4.939365	-6.469468
C	-10.545105	-4.895286	-7.851987
N	-11.177111	-5.623097	-8.848350
C	-11.646792	-6.917589	-8.771350
H	-11.995550	-7.260715	-9.759989
O	-11.679846	-7.619109	-7.789317
H	-10.995812	-5.280094	-9.784126
C	-9.457696	-4.007872	-8.106128
C	-9.004934	-3.518715	-6.851955
C	-7.961599	-2.618951	-6.645720
C	-7.443211	-2.109996	-5.459741
H	-6.631551	-1.405121	-5.597927
H	-7.482160	-2.267931	-7.549678
C	-8.868308	-3.650134	-9.392361
O	-7.872643	-2.978157	-9.563488
O	-9.575003	-4.140303	-10.462717

C	-9.039980	-3.827070	-11.763494
H	-9.013831	-2.749251	-11.914459
H	-9.714759	-4.296035	-12.474411
H	-8.033394	-4.228870	-11.868053
C	-11.945632	-5.580928	-5.776121
O	-11.909968	-6.012780	-4.643950
O	-13.073493	-5.551860	-6.514894
C	-14.204322	-6.244334	-5.954150
H	-14.470512	-5.824552	-4.985294
H	-13.973567	-7.302825	-5.842106
H	-15.011163	-6.101349	-6.667600
H	-10.457530	-4.519063	-3.853587
H	-8.989445	-3.242039	-2.630195
C	-6.652234	1.282796	1.582883
O	-7.793176	1.609644	1.334905
O	-6.170266	1.198389	2.839890
C	-7.036829	1.693868	3.876276
H	-7.979090	1.147840	3.882796
H	-7.230902	2.754568	3.724534
H	-6.495875	1.532135	4.804570
O	-1.827106	-0.538709	-1.750215
H	0.240134	-0.669293	-0.136207
H	0.462108	0.841991	0.793424
H	0.240214	0.892409	-0.980896

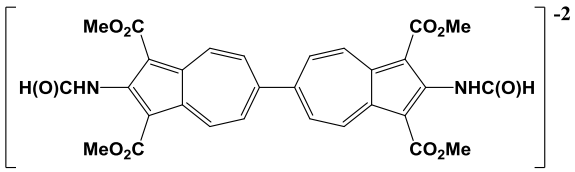
Table A3.5. Cartesian coordinates (Å) for the optimized structure of [2,2'-bisformamido-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1b'$^{-1}$).



Atom	x	y	z
C	-0.064073	0.805099	-0.288545
O	-1.450172	0.802900	0.068709
C	-2.319068	0.322955	-0.905449
C	-3.706573	0.354187	-0.495066
C	-4.264002	0.949377	0.675405
N	-3.508972	1.693830	1.591688
C	-3.840357	2.868060	2.204944
H	-2.973752	3.260259	2.770487
O	-4.903925	3.451077	2.177110
H	-2.518246	1.493248	1.554041
C	-5.648559	0.715755	0.700373
C	-5.991597	0.000668	-0.489221
C	-7.297700	-0.420362	-0.844694
H	-8.070570	-0.097973	-0.158586
C	-7.740463	-1.126397	-1.936181
H	-8.815967	-1.248727	-1.962283
C	-7.047804	-1.661085	-3.062454
C	-5.635984	-1.549361	-3.219200
H	-5.233654	-2.062369	-4.083627

C	-4.670654	-0.958156	-2.439296
H	-3.657821	-1.056531	-2.805903
C	-4.785532	-0.240424	-1.224523
C	-7.811336	-2.353376	-4.095576
C	-8.993350	-3.059277	-3.722667
C	-9.885206	-3.797516	-4.461435
C	-9.913912	-4.086200	-5.848993
C	-10.927003	-4.844683	-6.513526
C	-10.592165	-4.905885	-7.875663
N	-11.253349	-5.616872	-8.885557
C	-11.818747	-6.857783	-8.818622
H	-12.148046	-7.181545	-9.824128
O	-11.970187	-7.557530	-7.838923
H	-11.020587	-5.300540	-9.817853
C	-9.396148	-4.161048	-8.101354
C	-8.971913	-3.645156	-6.834481
C	-7.837305	-2.829764	-6.606725
C	-7.345031	-2.293450	-5.440274
H	-6.471284	-1.671352	-5.589832
H	-7.275891	-2.587222	-7.498469
C	-8.710558	-3.933369	-9.355197
O	-7.638697	-3.383355	-9.526166
O	-9.417141	-4.401723	-10.458546
C	-8.773312	-4.219944	-11.724038
H	-8.623296	-3.161330	-11.935729
H	-9.443229	-4.661057	-12.459499
H	-7.805932	-4.721938	-11.744482
C	-12.136514	-5.353387	-5.860665
O	-12.220824	-5.724962	-4.707032
O	-13.225048	-5.300030	-6.675352
C	-14.410637	-5.914258	-6.157653
H	-14.728212	-5.432811	-5.232390
H	-14.236385	-6.973843	-5.970905
H	-15.165391	-5.785302	-6.930485
H	-10.678739	-4.266297	-3.893542
H	-9.207802	-3.060740	-2.661345
C	-6.592624	1.025202	1.776312
O	-7.781363	1.240001	1.643137
O	-6.010932	0.973679	3.005551
C	-6.833278	1.405199	4.094272
H	-7.725619	0.784692	4.180153
H	-7.129265	2.444922	3.955911
H	-6.214703	1.303809	4.983529
O	-1.865315	-0.082106	-1.959431
H	0.289194	-0.208071	-0.480460
H	0.457637	1.231936	0.565876
H	0.107854	1.410498	-1.178479

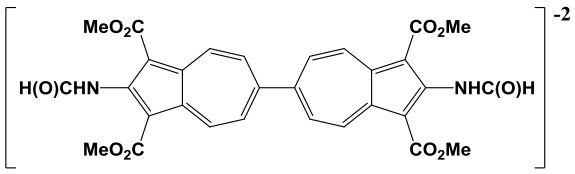
Table A3.6. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [2,2'-bisformamido-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-2}$ (III.1b'$^{-2}$).



Atom	x	y	z
C	-0.123419	1.180378	-0.478898
O	-1.468688	1.049630	-0.033793
C	-2.384595	0.604387	-1.012149
C	-3.732043	0.511465	-0.525187
C	-4.246518	0.972458	0.725607
N	-3.472155	1.695621	1.657540
C	-3.780318	2.803990	2.374443
H	-2.879747	3.161564	2.916393
O	-4.849503	3.381238	2.478079
H	-2.481188	1.517580	1.565408
C	-5.608318	0.643096	0.801370
C	-5.973429	-0.012089	-0.430921
C	-7.281769	-0.532245	-0.741190
H	-8.029589	-0.313683	0.010902
C	-7.739626	-1.208598	-1.829296
H	-8.800692	-1.411242	-1.773337
C	-7.103576	-1.636498	-3.065276
C	-5.684483	-1.389282	-3.262337
H	-5.273912	-1.832685	-4.159390
C	-4.735503	-0.769993	-2.508615
H	-3.738694	-0.779291	-2.929241
C	-4.826925	-0.110124	-1.232699
C	-7.850519	-2.301739	-4.069981
C	-9.140520	-2.898635	-3.762297
C	-10.025467	-3.619013	-4.503697
C	-9.988439	-4.032631	-5.883819
C	-11.031488	-4.761749	-6.563499
C	-10.629213	-4.943763	-7.895519
N	-11.283590	-5.674241	-8.909689
C	-11.904409	-6.878018	-8.849041
H	-12.201507	-7.199074	-9.869518
O	-12.152447	-7.566312	-7.873640
H	-11.007497	-5.389866	-9.839842
C	-9.359040	-4.317433	-8.081636
C	-8.977315	-3.744307	-6.811887
C	-7.795034	-2.960072	-6.565979
C	-7.333266	-2.376673	-5.426484
H	-6.426747	-1.809340	-5.591256
H	-7.179033	-2.805818	-7.441716
C	-8.590715	-4.227725	-9.290997
O	-7.453917	-3.813479	-9.449319
O	-9.295597	-4.671304	-10.432242
C	-8.564443	-4.621481	-11.651986
H	-8.290863	-3.596440	-11.909413

H	-9.228195	-5.032699	-12.412876
H	-7.650580	-5.215329	-11.592977
C	-12.303779	-5.142673	-5.969084
O	-12.524147	-5.389789	-4.796767
O	-13.331093	-5.143706	-6.883173
C	-14.562215	-5.684749	-6.412580
H	-14.954280	-5.108575	-5.571973
H	-14.432802	-6.722664	-6.102464
H	-15.248144	-5.630494	-7.257494
H	-10.892350	-3.977121	-3.962744
H	-9.444718	-2.808263	-2.728429
C	-6.495337	0.827751	1.939616
O	-7.705043	0.967388	1.914431
O	-5.828287	0.763597	3.140100
C	-6.597740	1.124666	4.282844
H	-7.454331	0.460187	4.411178
H	-6.953367	2.152422	4.197279
H	-5.921349	1.034426	5.132382
O	-1.947263	0.334265	-2.119088
H	0.284745	0.219118	-0.796872
H	0.436251	1.559888	0.376466
H	-0.047255	1.878035	-1.314733

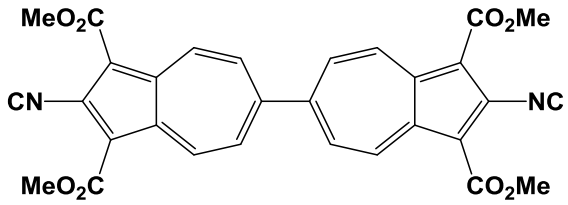
Table A3.7. Cartesian coordinates (Å) for the singlet state (T) optimized structure of [2,2'-bisformamido-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-2}$ (III.1b'$^{-2}$).



Atom	x	y	z
C	-0.035535	0.264598	0.155492
O	-1.427802	0.433442	0.394052
C	-2.275410	-0.028548	-0.640078
C	-3.665563	0.201533	-0.374408
C	-4.243064	0.953689	0.703332
N	-3.475914	1.691548	1.623827
C	-3.676257	2.932420	2.134124
H	-2.801603	3.232116	2.747935
O	-4.641007	3.669682	2.003279
H	-2.526239	1.352776	1.703183
C	-5.640845	0.881503	0.599097
C	-5.965728	0.108775	-0.566862
C	-7.303868	-0.196901	-1.003283
H	-8.083517	0.270136	-0.415198
C	-7.727222	-0.954080	-2.058702
H	-8.805984	-0.997520	-2.178294
C	-6.994912	-1.681137	-3.056696
C	-5.599383	-1.756432	-3.095017
H	-5.209291	-2.377981	-3.897167
C	-4.608399	-1.185714	-2.296821
H	-3.590441	-1.418914	-2.572818
C	-4.750099	-0.334433	-1.159881

C	-7.788920	-2.367621	-4.129205
C	-8.836503	-3.254874	-3.711213
C	-9.700607	-4.032294	-4.430344
C	-9.821352	-4.198402	-5.856411
C	-10.822948	-4.996953	-6.507117
C	-10.627230	-4.902153	-7.894037
N	-11.303136	-5.587813	-8.920229
C	-11.734456	-6.872374	-8.981174
H	-12.129713	-7.087765	-9.995453
O	-11.739668	-7.724000	-8.105920
H	-11.212802	-5.132986	-9.819118
C	-9.521091	-4.021652	-8.139856
C	-9.029168	-3.574086	-6.859854
C	-7.968486	-2.639787	-6.661121
C	-7.460491	-2.129348	-5.467320
H	-6.659702	-1.407356	-5.606336
H	-7.505042	-2.272494	-7.564634
C	-8.989127	-3.610292	-9.406493
O	-7.982966	-2.961062	-9.644650
O	-9.784450	-4.018028	-10.502501
C	-9.267834	-3.677011	-11.783522
H	-9.184467	-2.595292	-11.903868
H	-9.977603	-4.079303	-12.506818
H	-8.281116	-4.115788	-11.944428
C	-11.902566	-5.695385	-5.821222
O	-11.873364	-6.178195	-4.703870
O	-13.061846	-5.714671	-6.557469
C	-14.093761	-6.552387	-6.042508
H	-14.406893	-6.230458	-5.047775
H	-13.755669	-7.588434	-5.994117
H	-14.921521	-6.462875	-6.745189
H	-10.386758	-4.635805	-3.850309
H	-8.948651	-3.335544	-2.633526
C	-6.618115	1.399484	1.547587
O	-7.756349	1.760101	1.308816
O	-6.147702	1.387723	2.837969
C	-6.971024	2.053798	3.791176
H	-7.958696	1.592994	3.853874
H	-7.083431	3.106788	3.529544
H	-6.451335	1.959119	4.744147
O	-1.754090	-0.570421	-1.601887
H	0.224055	-0.789819	0.045258
H	0.467692	0.684257	1.026965
H	0.279951	0.790152	-0.747944

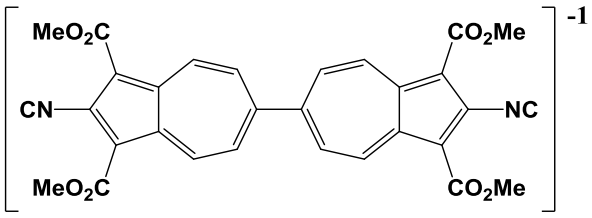
Table A3.8. Cartesian coordinates (Å) for the optimized structure of 2,2'-diisocyano-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl (III.1c').



Atom	x	y	z
C	-0.000253	0.048899	0.019408
O	-0.701113	0.008609	1.276281
C	-1.693100	-0.891559	1.379210
C	-2.363379	-0.857036	2.690811
C	-2.130737	0.030120	3.770193
N	-1.211342	1.036933	3.762214
C	-0.411090	1.892947	3.760971
C	-2.988137	-0.269006	4.857136
C	-3.785908	-1.374879	4.463641
C	-4.770031	-1.985134	5.242591
H	-4.907905	-1.539580	6.219259
C	-5.591085	-3.066350	4.954575
H	-6.286072	-3.321046	5.746345
C	-5.678479	-3.858347	3.801897
C	-4.913525	-3.704552	2.638088
H	-5.108298	-4.428394	1.855281
C	-3.918640	-2.786219	2.331462
H	-3.474178	-2.887765	1.349710
C	-3.392705	-1.745197	3.097941
C	-6.681390	-4.972787	3.819232
C	-6.665038	-5.821974	4.933761
C	-7.459269	-6.917987	5.239922
C	-8.512162	-7.489788	4.523997
C	-9.272634	-8.616338	4.932415
C	-10.223311	-8.865423	3.912594
N	-11.148217	-9.866734	3.943827
C	-11.950368	-10.720300	3.977288
C	-10.088060	-7.924679	2.862000
C	-9.026549	-7.053087	3.219414
C	-8.568574	-5.975028	2.461004
C	-7.548428	-5.070514	2.722673
H	-7.423438	-4.308224	1.962682
H	-9.101884	-5.823211	1.531241
C	-10.875565	-7.826984	1.620432
O	-10.723445	-6.969276	0.771503
O	-11.796746	-8.798620	1.510214
C	-12.610932	-8.778761	0.323305
H	-13.163024	-7.842293	0.254320
H	-13.290244	-9.618661	0.432663
H	-11.991460	-8.896817	-0.564987
C	-9.075582	-9.349631	6.194615

O	-8.273853	-9.038528	7.054499
O	-9.880774	-10.418742	6.310460
C	-9.756547	-11.183261	7.523921
H	-9.987785	-10.563932	8.389648
H	-8.746070	-11.577561	7.624459
H	-10.476871	-11.989451	7.425274
H	-7.236012	-7.410344	6.177513
H	-5.900222	-5.605913	5.670934
C	-3.072458	0.405114	6.164449
O	-3.829560	0.081864	7.059639
O	-2.215494	1.433424	6.278832
C	-2.231374	2.143032	7.531417
H	-1.969869	1.474828	8.351004
H	-3.216711	2.569002	7.716212
H	-1.487351	2.926042	7.422060
O	-1.988144	-1.647335	0.473187
H	0.467721	-0.912637	-0.187655
H	0.749774	0.824714	0.139037
H	-0.685022	0.296670	-0.790715

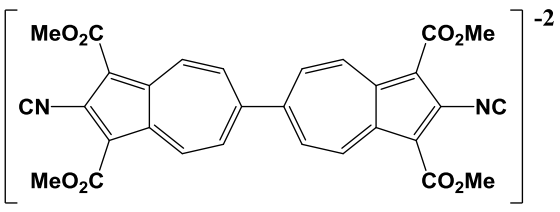
Table A3.9. Cartesian coordinates (Å) for the optimized structure of [2,2'-diisocyano-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1c'$^{-1}$).



Atom	x	y	z
C	-0.378631	0.390226	-0.160153
O	-0.907284	0.218152	1.158267
C	-2.000953	-0.579393	1.264069
C	-2.497854	-0.685783	2.634895
C	-2.106586	0.078668	3.763139
N	-1.188279	1.092315	3.744300
C	-0.398413	1.955956	3.727631
C	-2.838148	-0.341665	4.903767
C	-3.701105	-1.397047	4.481936
C	-4.603049	-2.107700	5.313784
H	-4.625576	-1.761706	6.338083
C	-5.457607	-3.142809	5.024136
H	-6.059219	-3.450193	5.870096
C	-5.732439	-3.835805	3.809916
C	-5.090826	-3.512783	2.579619
H	-5.357363	-4.148626	1.744906
C	-4.139226	-2.574015	2.264623
H	-3.816032	-2.571692	1.232476
C	-3.494169	-1.606428	3.076228
C	-6.708252	-4.921078	3.830580
C	-6.849793	-5.686374	5.024044
C	-7.663789	-6.746068	5.340207
C	-8.649241	-7.412821	4.569164
C	-9.442544	-8.514308	5.009330

C	-10.274338	-8.888325	3.922586
N	-11.213583	-9.882423	3.953190
C	-12.022184	-10.728292	3.978672
C	-10.021768	-8.042470	2.813230
C	-9.009898	-7.118998	3.209965
C	-8.455992	-6.102055	2.391642
C	-7.478079	-5.175450	2.658667
H	-7.302657	-4.489813	1.839646
H	-8.898474	-6.036851	1.406611
C	-10.658496	-8.079428	1.497444
O	-10.571723	-7.220099	0.637462
O	-11.382880	-9.209227	1.294178
C	-12.068261	-9.302270	0.042056
H	-12.759530	-8.468811	-0.086662
H	-12.610752	-10.243642	0.082405
H	-11.361491	-9.303574	-0.788494
C	-9.386522	-9.110015	6.342858
O	-8.721039	-8.703515	7.279755
O	-10.168594	-10.213480	6.463427
C	-10.179515	-10.838815	7.750124
H	-10.532828	-10.147413	8.515961
H	-9.182075	-11.185167	8.023131
H	-10.862062	-11.679318	7.653382
H	-7.532646	-7.149223	6.335096
H	-6.160741	-5.424697	5.817140
C	-2.754803	0.181671	6.266346
O	-3.442863	-0.168450	7.209703
O	-1.799754	1.136156	6.410392
C	-1.670620	1.704002	7.717361
H	-1.401000	0.940821	8.448384
H	-2.602395	2.175861	8.030825
H	-0.878893	2.443796	7.629978
O	-2.475372	-1.134086	0.288017
H	-0.047244	-0.563164	-0.573388
H	0.462986	1.068507	-0.044295
H	-1.126452	0.821548	-0.826534

Table A3.10. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [2,2'-diisocyano-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-2}$ (III.1c'$^{-2}$).

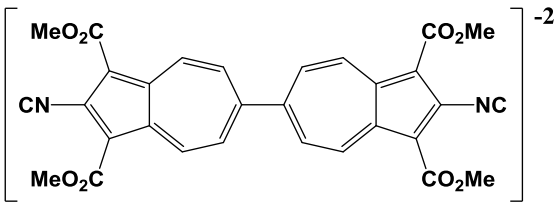


Atom	x	y	z
C	-0.567240	0.598225	-0.220614
O	-0.987881	0.342269	1.114157
C	-2.105972	-0.443584	1.247807
C	-2.516050	-0.616947	2.629992
C	-2.039327	0.090583	3.767120
N	-1.107027	1.093601	3.747235
C	-0.304027	1.945426	3.729885

C	-2.701105	-0.404829	4.924578
C	-3.594094	-1.442939	4.493739
C	-4.459399	-2.213468	5.350566
H	-4.405022	-1.930849	6.392862
C	-5.332711	-3.218114	5.068855
H	-5.869666	-3.556409	5.944898
C	-5.735813	-3.859884	3.830661
C	-5.153048	-3.426151	2.574033
H	-5.471639	-3.994521	1.710625
C	-4.219360	-2.487277	2.261662
H	-3.966106	-2.422978	1.212283
C	-3.492760	-1.560930	3.092487
C	-6.696147	-4.904881	3.849179
C	-6.969822	-5.620728	5.082226
C	-7.806809	-6.648176	5.389835
C	-8.753532	-7.372450	4.580426
C	-9.572078	-8.461323	5.030417
C	-10.327492	-8.913032	3.914731
N	-11.286799	-9.890281	3.948979
C	-12.111797	-10.720335	3.981559
C	-9.991379	-8.119330	2.783370
C	-9.003990	-7.168465	3.207699
C	-8.366267	-6.190534	2.363292
C	-7.406085	-5.265638	2.635250
H	-7.178569	-4.643610	1.780234
H	-8.737119	-6.183349	1.347361
C	-10.534122	-8.225778	1.441000
O	-10.370504	-7.447119	0.513565
O	-11.297972	-9.352695	1.260425
C	-11.907355	-9.489788	-0.017231
H	-12.561003	-8.643264	-0.238748
H	-12.488686	-10.408918	0.037361
H	-11.159040	-9.560382	-0.809357
C	-9.600806	-8.986508	6.383659
O	-9.123227	-8.473164	7.383930
O	-10.234486	-10.201614	6.472952
C	-10.345971	-10.745937	7.782567
H	-10.893873	-10.074045	8.446574
H	-9.362856	-10.934161	8.219624
H	-10.890767	-11.680877	7.661877
H	-7.755722	-6.990852	6.414494
H	-6.347118	-5.330050	5.917725
C	-2.533266	0.041216	6.296009
O	-3.010666	-0.465460	7.300126
O	-1.746659	1.161893	6.404837
C	-1.518897	1.632012	7.727998
H	-1.021154	0.875563	8.338724
H	-2.455029	1.907733	8.218477
H	-0.878987	2.505978	7.617569
O	-2.637838	-0.918335	0.255717
H	-0.299589	-0.326218	-0.737099

H	0.303165	1.245964	-0.129973
H	-1.350359	1.098027	-0.794890

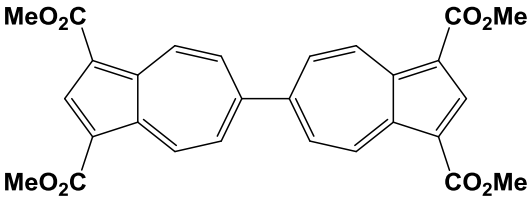
Table A3.11. Cartesian coordinates (Å) for the triplet state (T) optimized structure of [2,2'-diisocyano-1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-2}$ (III.1c'$^{-2}$).



Atom	x	y	z
C	-0.004656	0.091608	0.015482
O	-0.643881	0.033396	1.284796
C	-1.730913	-0.801271	1.369151
C	-2.363707	-0.777123	2.674918
C	-2.074751	0.105177	3.761532
N	-1.168344	1.122887	3.740606
C	-0.382896	1.994654	3.723399
C	-2.935200	-0.227436	4.853895
C	-3.759095	-1.320864	4.440247
C	-4.766705	-1.949631	5.244493
H	-4.894687	-1.513162	6.224235
C	-5.593959	-3.012249	4.948675
H	-6.283016	-3.268200	5.749016
C	-5.716284	-3.822451	3.795911
C	-4.942099	-3.636978	2.626149
H	-5.148288	-4.353418	1.835546
C	-3.963582	-2.720173	2.306383
H	-3.540484	-2.810688	1.316347
C	-3.405543	-1.660734	3.096861
C	-6.718595	-4.940581	3.819353
C	-6.715144	-5.814156	4.931704
C	-7.505617	-6.896408	5.255138
C	-8.592446	-7.486880	4.528726
C	-9.348109	-8.624200	4.953829
C	-10.300524	-8.919814	3.929581
N	-11.251789	-9.894825	3.979871
C	-12.075853	-10.729209	4.023192
C	-10.140712	-7.966770	2.877273
C	-9.089030	-7.074531	3.252248
C	-8.622760	-5.967599	2.468099
C	-7.615922	-5.063698	2.731896
H	-7.498265	-4.301206	1.966974
H	-9.162623	-5.813608	1.544594
C	-10.888119	-7.898811	1.635096
O	-10.886206	-6.988414	0.818902
O	-11.649444	-9.018462	1.408862
C	-12.456019	-8.994064	0.237514
H	-13.153576	-8.153898	0.252856
H	-13.002281	-9.935918	0.243654
H	-11.845013	-8.915945	-0.664419
C	-9.158892	-9.324761	6.209516

O	-8.398604	-9.022037	7.118196
O	-9.945710	-10.444677	6.323528
C	-9.827622	-11.160808	7.546539
H	-10.089986	-10.533836	8.401479
H	-8.810966	-11.532003	7.693885
H	-10.525106	-11.992370	7.462221
H	-7.276424	-7.381998	6.192438
H	-5.943272	-5.598643	5.665844
C	-2.983304	0.400854	6.160842
O	-3.742335	0.135131	7.082184
O	-2.044378	1.391157	6.316246
C	-2.039233	2.045487	7.579182
H	-1.823544	1.344865	8.388985
H	-3.000583	2.520761	7.785775
H	-1.253605	2.796084	7.511358
O	-2.061722	-1.467949	0.398911
H	0.394827	-0.882819	-0.274106
H	0.803225	0.811956	0.132308
H	-0.695548	0.423575	-0.762610

Table A3.12. Cartesian coordinates (Å) for the optimized structure of 1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl (III.1d').

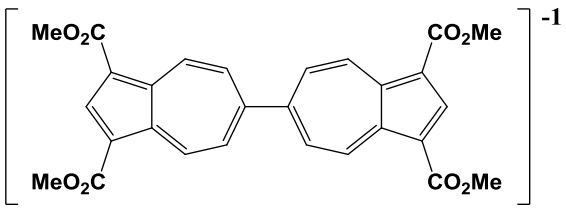


Atom	x	y	z
C	-0.052906	0.223820	0.125631
O	-1.471261	0.372409	0.303407
C	-2.250800	-0.193741	-0.650675
C	-3.675808	0.022295	-0.387795
C	-4.206427	0.743812	0.688971
C	-5.605469	0.753272	0.623514
C	-5.997657	0.015209	-0.526812
C	-7.302925	-0.208869	-0.954887
H	-8.065095	0.246469	-0.333723
C	-7.764840	-0.921516	-2.055535
H	-8.842412	-0.920976	-2.169633
C	-7.058448	-1.615841	-3.047449
C	-5.665314	-1.736770	-3.143356
H	-5.308904	-2.335552	-3.973385
C	-4.660440	-1.230507	-2.326669
H	-3.646305	-1.474446	-2.619740
C	-4.759589	-0.455830	-1.174428
C	-7.871811	-2.296023	-4.111043
C	-8.920191	-3.118898	-3.677209
C	-9.833035	-3.872283	-4.407087
C	-9.959518	-4.021530	-5.785286
C	-10.926754	-4.816938	-6.459427
C	-10.700879	-4.700087	-7.836793
C	-9.613780	-3.851185	-8.079143

C	-9.118368	-3.400359	-6.824740
C	-8.050403	-2.530207	-6.627213
C	-7.507358	-2.048242	-5.441302
H	-6.682297	-1.358332	-5.573981
H	-7.581029	-2.179171	-7.538327
C	-9.081146	-3.502282	-9.398474
O	-8.121521	-2.787217	-9.612773
O	-9.791320	-4.081783	-10.397389
C	-9.335248	-3.809475	-11.732860
H	-9.365737	-2.740137	-11.939155
H	-10.020583	-4.343412	-12.385406
H	-8.316212	-4.169918	-11.871376
H	-11.279483	-5.193746	-8.600686
C	-11.978604	-5.622212	-5.833892
O	-12.173486	-5.736422	-4.639345
O	-12.744126	-6.253947	-6.757751
C	-13.807302	-7.071032	-6.241872
H	-14.510199	-6.468637	-5.667157
H	-13.410767	-7.860673	-5.604089
H	-14.294019	-7.495401	-7.115583
H	-10.552286	-4.435822	-3.824984
H	-9.029964	-3.200575	-2.602322
C	-6.499644	1.406845	1.582643
O	-7.714238	1.421511	1.528993
O	-5.810237	2.013506	2.579785
C	-6.601488	2.672336	3.582210
H	-7.269720	1.963949	4.070934
H	-7.192914	3.473496	3.139964
H	-5.886655	3.075496	4.294142
H	-3.622122	1.223625	1.457439
O	-1.784543	-0.799046	-1.596338
H	0.224707	-0.829711	0.113127
H	0.397775	0.726701	0.976674
H	0.267564	0.687292	-0.806954

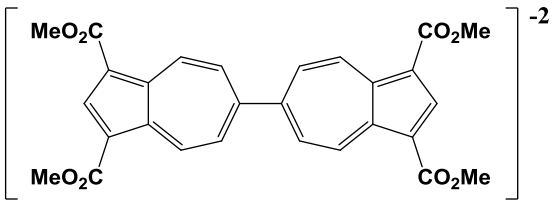
Table A3.13. Cartesian coordinates (Å) for the optimized structure of [1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1d'$^{-1}$).

Atom	x	y	z
C	-0.056224	0.726692	-0.132120
O	-1.455788	0.730328	0.151444
C	-2.251319	0.124451	-0.791404
C	-3.657571	0.173908	-0.432007
C	-4.175006	0.763174	0.730808
C	-5.570323	0.621681	0.742996
C	-5.954908	-0.080056	-0.446174
C	-7.276329	-0.425634	-0.818163
H	-8.035285	-0.093216	-0.120995



C	-7.741138	-1.095055	-1.924952
H	-8.820574	-1.172826	-1.960862
C	-7.064754	-1.641243	-3.055855
C	-5.649101	-1.572446	-3.218679
H	-5.268824	-2.074585	-4.099355
C	-4.663258	-1.035466	-2.425205
H	-3.651449	-1.157108	-2.791285
C	-4.754670	-0.357869	-1.185669
C	-7.856039	-2.298714	-4.092150
C	-9.051041	-2.978106	-3.710701
C	-9.975473	-3.683173	-4.444629
C	-10.033761	-3.942746	-5.835028
C	-11.048789	-4.696215	-6.511238
C	-10.734936	-4.717673	-7.877933
C	-9.549468	-4.000595	-8.094509
C	-9.090368	-3.509819	-6.828414
C	-7.923509	-2.739128	-6.608141
C	-7.399838	-2.233834	-5.441968
H	-6.507210	-1.638986	-5.591100
H	-7.370029	-2.504503	-7.508513
C	-8.914200	-3.802399	-9.385026
O	-7.887391	-3.187409	-9.616128
O	-9.613502	-4.405400	-10.402758
C	-9.049697	-4.259303	-11.706483
H	-8.987419	-3.208426	-11.992672
H	-9.721337	-4.793096	-12.375835
H	-8.048630	-4.690869	-11.752959
H	-11.314212	-5.207998	-8.642284
C	-12.206170	-5.333829	-5.908387
O	-12.519617	-5.335661	-4.730215
O	-12.978251	-5.987128	-6.839015
C	-14.133293	-6.649111	-6.322962
H	-14.809335	-5.942243	-5.839524
H	-13.856174	-7.414841	-5.596452
H	-14.616745	-7.105250	-7.184471
H	-10.782759	-4.127013	-3.875581
H	-9.247279	-2.987618	-2.645813
C	-6.452390	1.108032	1.788955
O	-7.666439	1.008086	1.837792
O	-5.760377	1.736588	2.796080
C	-6.557612	2.243961	3.866187
H	-7.124124	1.445615	4.347723
H	-7.258563	3.000746	3.509983
H	-5.854483	2.685065	4.569874
H	-3.591551	1.248114	1.495595
O	-1.760567	-0.376175	-1.788727
H	0.325630	-0.291886	-0.215678
H	0.412187	1.237310	0.706887
H	0.157740	1.254190	-1.062919

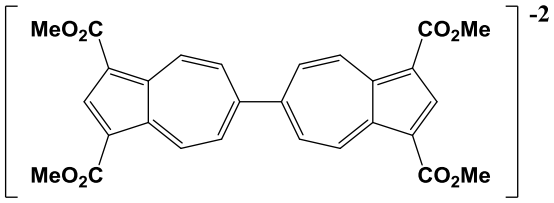
Table A3.14. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1d'$^{-2}$).



Atom	x	y	z
C	-0.087608	1.073204	-0.266018
O	-1.461756	0.990758	0.079358
C	-2.271409	0.355449	-0.864094
C	-3.648392	0.290999	-0.446191
C	-4.139839	0.787420	0.772467
C	-5.521139	0.539478	0.834684
C	-5.909643	-0.136409	-0.384825
C	-7.240843	-0.572689	-0.722488
H	-7.984040	-0.330933	0.027480
C	-7.715535	-1.213601	-1.825543
H	-8.787411	-1.359144	-1.792502
C	-7.085180	-1.657498	-3.059925
C	-5.657025	-1.452200	-3.253737
H	-5.264668	-1.875536	-4.168912
C	-4.686807	-0.899281	-2.475572
H	-3.686264	-0.934731	-2.888863
C	-4.758178	-0.284196	-1.175185
C	-7.855570	-2.287379	-4.069008
C	-9.148588	-2.873324	-3.747252
C	-10.068703	-3.550061	-4.488327
C	-10.083826	-3.894699	-5.887116
C	-11.129073	-4.625659	-6.571675
C	-10.761877	-4.746232	-7.922037
C	-9.520577	-4.116107	-8.108395
C	-9.091716	-3.586154	-6.831947
C	-7.866863	-2.869254	-6.584256
C	-7.357080	-2.348144	-5.435060
H	-6.424586	-1.822344	-5.594594
H	-7.264659	-2.712065	-7.470544
C	-8.828054	-4.023860	-9.367614
O	-7.763678	-3.476707	-9.617831
O	-9.519743	-4.661788	-10.398884
C	-8.895187	-4.597901	-11.671459
H	-8.781321	-3.566019	-12.013096
H	-9.551070	-5.144019	-12.350092
H	-7.904794	-5.059783	-11.658523
H	-11.337062	-5.238866	-8.687540
C	-12.340951	-5.156231	-6.001521
O	-12.727539	-5.108775	-4.842434
O	-13.133984	-5.801454	-6.952261
C	-14.335406	-6.365629	-6.449538
H	-14.986901	-5.604271	-6.012979
H	-14.137342	-7.118774	-5.682583
H	-14.825526	-6.828076	-7.306745

H	-10.930541	-3.909608	-3.939525
H	-9.414797	-2.822507	-2.699645
C	-6.373171	0.915757	1.932931
O	-7.577845	0.749122	2.059631
O	-5.667646	1.554099	2.954497
C	-6.454079	1.967699	4.060827
H	-6.957761	1.122576	4.536194
H	-7.217343	2.692120	3.764368
H	-5.758147	2.429296	4.761995
H	-3.554543	1.275533	1.533349
O	-1.763169	-0.064115	-1.894082
H	0.357354	0.082132	-0.387588
H	0.393570	1.597423	0.560151
H	0.061988	1.626252	-1.196541

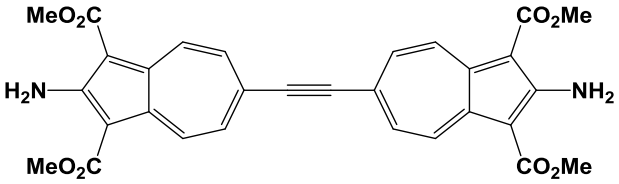
Table A3.15. Cartesian coordinates (Å) for the triplet state (T) optimized structure of [1,1',3,3'-tetramethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1d'$^{-2}$).



Atom	x	y	z
C	-0.116538	-0.304982	0.612343
O	-1.486046	0.064949	0.657806
C	-2.289500	-0.521106	-0.322192
C	-3.665829	-0.107769	-0.214213
C	-4.157524	0.779974	0.758519
C	-5.540103	0.938582	0.558986
C	-5.932865	0.127323	-0.569924
C	-7.271989	0.017789	-1.090686
H	-8.011412	0.609929	-0.568007
C	-7.727616	-0.731088	-2.153083
H	-8.793473	-0.634212	-2.346428
C	-7.058980	-1.605945	-3.048225
C	-5.668247	-1.882901	-3.000770
H	-5.331871	-2.580147	-3.765083
C	-4.672099	-1.433465	-2.162984
H	-3.677476	-1.814069	-2.352223
C	-4.768555	-0.521706	-1.050597
C	-7.876525	-2.286810	-4.115444
C	-8.804294	-3.280152	-3.707478
C	-9.673107	-4.072284	-4.424283
C	-9.889140	-4.118959	-5.848720
C	-10.822211	-4.992864	-6.522137
C	-10.741461	-4.745399	-7.903348
C	-9.784233	-3.739248	-8.121513
C	-9.243508	-3.341261	-6.841878
C	-8.232966	-2.333548	-6.642079
C	-7.665232	-1.900470	-5.463612
H	-6.919245	-1.118289	-5.585196
H	-7.881117	-1.858867	-7.548007

C	-9.434345	-3.215116	-9.417653
O	-8.628080	-2.341477	-9.701788
O	-10.152533	-3.831750	-10.443886
C	-9.876928	-3.344540	-11.748108
H	-10.119761	-2.282681	-11.840586
H	-10.505910	-3.928467	-12.420615
H	-8.825134	-3.474933	-12.014065
H	-11.316678	-5.241545	-8.666109
C	-11.696928	-5.966327	-5.918334
O	-11.836678	-6.245564	-4.736632
O	-12.460094	-6.646763	-6.869221
C	-13.342507	-7.625774	-6.344394
H	-14.060802	-7.188711	-5.646195
H	-12.800717	-8.417218	-5.820154
H	-13.866521	-8.042753	-7.204878
H	-10.278697	-4.761687	-3.851403
H	-8.826769	-3.446599	-2.632735
C	-6.389176	1.779938	1.364620
O	-7.589466	1.985568	1.258751
O	-5.681105	2.417188	2.385127
C	-6.455213	3.271450	3.213292
H	-7.266472	2.729608	3.705217
H	-6.894891	4.094619	2.644162
H	-5.763918	3.664838	3.959265
H	-3.574309	1.257821	1.527111
O	-1.778721	-1.284918	-1.128121
H	0.014033	-1.383133	0.735043
H	0.359558	0.222857	1.439119
H	0.348384	-0.013643	-0.332988

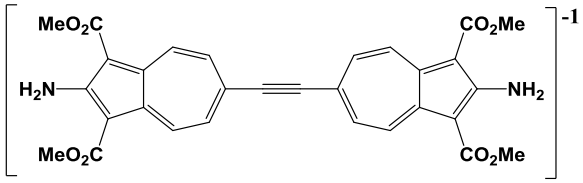
Table A3.16. Cartesian coordinates (Å) for the optimized structure of bis(2-amino-1,3-dimethoxycarbonyl-6-azulenyl)acetylene (III.2a').



Atom	x	y	z
C	0.036414	0.004892	0.063278
O	-0.300360	-0.342861	1.418195
C	-1.227048	-1.349099	1.562457
C	-1.517601	-1.652653	2.954049
C	-0.958014	-1.020503	4.109792
C	-1.518329	-1.621299	5.281806
C	-2.423963	-2.629516	4.865103
C	-3.175581	-3.451962	5.712432
C	-4.073778	-4.460108	5.409284
C	-4.499440	-4.955525	4.161815
C	-5.442488	-6.018097	4.176016
C	-6.248943	-6.922408	4.188148
C	-7.192690	-7.984353	4.202476
C	-7.621828	-8.443199	5.462644
C	-8.521863	-9.441243	5.792494

C	-9.271960	-10.287419	4.967424
C	-10.180171	-11.281929	5.410731
C	-10.736567	-11.917149	4.255136
N	-11.635958	-12.907856	4.268421
H	-11.960226	-13.279889	3.390978
H	-11.967861	-13.249474	5.155354
C	-10.172379	-11.320056	3.083094
C	-9.267505	-10.311077	3.499613
C	-8.513063	-9.491312	2.652190
C	-7.615201	-8.482804	2.955147
H	-7.165391	-7.997588	2.096762
H	-8.662043	-9.680013	1.597581
C	-10.457418	-11.665631	1.700147
O	-9.972149	-11.154342	0.710490
O	-11.376595	-12.682247	1.583135
C	-11.705280	-13.074290	0.238416
H	-12.142178	-12.239391	-0.307917
H	-12.426289	-13.881360	0.339554
H	-10.816679	-13.420511	-0.287716
C	-10.475415	-11.581015	6.802304
O	-9.991711	-11.041973	7.777894
O	-11.404105	-12.585396	6.946635
C	-11.745830	-12.928463	8.301505
H	-12.182552	-12.072556	8.814429
H	-10.863522	-13.260463	8.847025
H	-12.470441	-13.734754	8.222625
H	-8.676632	-9.596323	6.851738
H	-7.176430	-7.931152	6.307699
C	-4.074070	-4.493089	2.901680
C	-3.175714	-3.493471	2.571991
C	-2.423833	-2.649033	3.397225
H	-3.024082	-3.335388	1.512735
H	-4.521464	-5.003198	2.056505
H	-4.520901	-4.947884	6.267621
H	-3.023685	-3.266065	6.767121
C	-1.229353	-1.279550	6.664892
O	-1.711336	-1.794004	7.654515
O	-0.310064	-0.263051	6.782096
C	0.022922	0.124845	8.126958
H	0.462784	-0.711377	8.668875
H	-0.864207	0.468172	8.657445
H	0.742599	0.933128	8.025993
N	-0.058912	-0.029532	4.096650
H	0.269363	0.315511	3.209691
H	0.267166	0.340730	4.974171
O	-1.713278	-1.885716	0.586789
H	0.472338	-0.848890	-0.453851
H	0.760401	0.811731	0.142280
H	-0.848100	0.337655	-0.478188

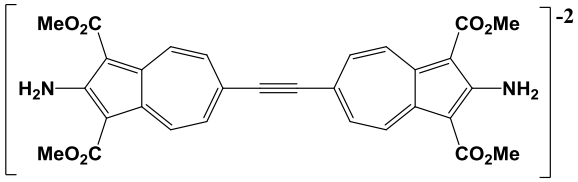
Table A3.17. Cartesian coordinates (Å) for the optimized structure of [bis(2-amino-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-1}$ (III.2a'$^{-1}$).



Atom	x	y	z
C	0.054625	0.009415	0.071777
O	-0.272148	-0.320662	1.424268
C	-1.211153	-1.338454	1.578928
C	-1.499604	-1.634944	2.958779
C	-0.941095	-1.001433	4.109489
C	-1.503764	-1.600376	5.276605
C	-2.420641	-2.620029	4.846647
C	-3.182263	-3.449181	5.709266
C	-4.073513	-4.450393	5.417471
C	-4.514218	-4.968606	4.162371
C	-5.438608	-6.011898	4.176374
C	-6.253509	-6.927980	4.188745
C	-7.178452	-7.970783	4.202684
C	-7.623158	-8.451776	5.471072
C	-8.515980	-9.443432	5.789367
C	-9.275404	-10.297310	4.949175
C	-10.194618	-11.303136	5.406009
C	-10.753377	-11.936337	4.255250
N	-11.662552	-12.937435	4.268585
H	-11.986878	-13.304150	3.391444
H	-11.991524	-13.276637	5.155047
C	-10.190470	-11.337526	3.088182
C	-9.273138	-10.318318	3.518220
C	-8.511167	-9.489418	2.655665
C	-7.619427	-8.488666	2.947541
H	-7.171402	-8.004748	2.086361
H	-8.665460	-9.682284	1.602710
C	-10.473443	-11.675732	1.716763
O	-10.000654	-11.176494	0.709571
O	-11.405652	-12.703522	1.589706
C	-11.723730	-13.078537	0.246939
H	-12.156139	-12.240915	-0.301447
H	-12.448346	-13.886440	0.331881
H	-10.835642	-13.422742	-0.284091
C	-10.483356	-11.599471	6.785832
O	-10.010168	-11.073891	7.779328
O	-11.423055	-12.616635	6.940405
C	-11.750054	-12.946605	8.292868
H	-12.182071	-12.089809	8.811098
H	-10.866379	-13.276593	8.840019
H	-12.477478	-13.753978	8.230080
H	-8.673366	-9.605413	6.847053
H	-7.177689	-7.942859	6.319128
C	-4.069751	-4.487492	2.893944

C	-3.177422	-3.495418	2.575567
C	-2.418372	-2.641143	3.415693
H	-3.020133	-3.333429	1.517868
H	-4.514975	-4.996691	2.045928
H	-4.521320	-4.934444	6.278690
H	-3.028091	-3.256132	6.762205
C	-1.221069	-1.261824	6.647997
O	-1.693616	-1.761224	7.655223
O	-0.289643	-0.233319	6.774974
C	0.028184	0.142014	8.117713
H	0.461669	-0.695126	8.665990
H	-0.860229	0.485133	8.648894
H	0.751843	0.950767	8.032703
N	-0.032073	-0.000198	4.096081
H	0.295930	0.339830	3.209577
H	0.291284	0.367467	4.973181
O	-1.684038	-1.864388	0.585475
H	0.487109	-0.847166	-0.446417
H	0.781596	0.817201	0.134497
H	-0.829252	0.338873	-0.475368

Table A3.18. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [bis(2-amino-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-2}$ (III.2a'$^{-2}$).

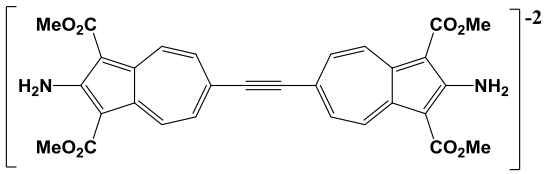


Atom	x	y	z
C	0.082464	0.037864	0.084994
O	-0.236522	-0.280246	1.433450
C	-1.190947	-1.312889	1.593518
C	-1.478265	-1.607627	2.961198
C	-0.918595	-0.974577	4.109244
C	-1.482112	-1.573383	5.273724
C	-2.411873	-2.603918	4.829814
C	-3.184398	-3.443485	5.709487
C	-4.068651	-4.437580	5.427432
C	-4.527747	-4.979400	4.162593
C	-5.433137	-6.004656	4.176246
C	-6.258720	-6.935474	4.188561
C	-7.164681	-7.960226	4.202226
C	-7.627893	-8.464405	5.481006
C	-8.513610	-9.449265	5.789423
C	-9.283688	-10.314268	4.932483
C	-10.215773	-11.330553	5.403601
C	-10.775339	-11.963692	4.255554
N	-11.692019	-12.974082	4.269169
H	-12.018722	-13.333069	3.391221
H	-12.023488	-13.305163	5.156282
C	-10.211402	-11.365262	3.091085
C	-9.281406	-10.334946	3.534999

C	-8.508492	-9.495736	2.655331
C	-7.623844	-8.501995	2.937391
H	-7.175758	-8.020495	2.073276
H	-8.666100	-9.694928	1.603716
C	-10.493703	-11.701161	1.731811
O	-10.034655	-11.219335	0.704408
O	-11.442633	-12.742767	1.599892
C	-11.752703	-13.106168	0.260878
H	-12.183294	-12.268244	-0.291728
H	-12.479718	-13.915875	0.333717
H	-10.865670	-13.448955	-0.276075
C	-10.503891	-11.624557	6.771273
O	-10.045055	-11.114954	7.785262
O	-11.459587	-12.656014	6.931333
C	-11.779055	-12.973658	8.279788
H	-12.211162	-12.116632	8.801031
H	-10.896334	-13.299930	8.833814
H	-12.507552	-13.783712	8.229391
H	-8.674632	-9.617195	6.845951
H	-7.182659	-7.957452	6.331998
C	-4.065004	-4.474797	2.883811
C	-3.179732	-3.489540	2.575388
C	-2.409749	-2.624456	3.432329
H	-3.019068	-3.321287	1.518858
H	-4.510273	-4.981718	2.032817
H	-4.516396	-4.919390	6.291551
H	-3.026726	-3.244355	6.761103
C	-1.200154	-1.237180	6.632995
O	-1.658741	-1.719449	7.660395
O	-0.252430	-0.194478	6.764912
C	0.057356	0.169158	8.103930
H	0.489611	-0.668130	8.656209
H	-0.830137	0.510211	8.641214
H	0.782929	0.980157	8.031087
N	-0.001406	0.035338	4.095625
H	0.326704	0.369528	3.208431
H	0.322390	0.397047	4.973530
O	-1.649519	-1.822722	0.579521
H	0.515368	-0.818672	-0.436386
H	0.810153	0.848646	0.135394
H	-0.800645	0.363309	-0.468905

Table A3.19. Cartesian coordinates (Å) for the triplet state (T) optimized structure of [bis(2-amino-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-2}$ (III.2a'$^{-2}$).

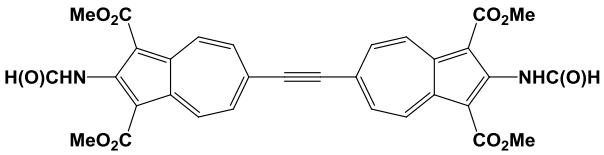
Atom	x	y	z
C	0.085697	0.047232	0.085583
O	-0.234281	-0.274858	1.434123



C	-1.187653	-1.304724	1.591185
C	-1.474349	-1.602308	2.960879
C	-0.913881	-0.970634	4.109725
C	-1.476303	-1.571197	5.274245
C	-2.403923	-2.599154	4.833436
C	-3.172194	-3.436681	5.712426
C	-4.059790	-4.434213	5.418182
C	-4.507732	-4.958763	4.160362
C	-5.436654	-6.007601	4.173803
C	-6.250239	-6.922243	4.185834
C	-7.189454	-7.980972	4.200331
C	-7.617571	-8.440601	5.467626
C	-8.543974	-9.467467	5.787558
C	-9.278978	-10.297399	4.975577
C	-10.217898	-11.326998	5.417217
C	-10.762851	-11.949700	4.255862
N	-11.671459	-12.954483	4.270079
H	-11.991425	-13.317685	3.389390
H	-11.996687	-13.288068	5.160538
C	-10.212184	-11.364871	3.077528
C	-9.275916	-10.320925	3.490121
C	-8.538283	-9.516500	2.655284
C	-7.613489	-8.479398	2.946512
H	-7.169695	-7.997627	2.083267
H	-8.687791	-9.702350	1.598919
C	-10.503421	-11.713840	1.731579
O	-10.049090	-11.235529	0.695845
O	-11.453836	-12.769645	1.605583
C	-11.764042	-13.135641	0.269866
H	-12.202856	-12.302327	-0.284313
H	-12.485160	-13.951364	0.343319
H	-10.876637	-13.472434	-0.271270
C	-10.516828	-11.630855	6.772310
O	-10.065237	-11.120782	7.793987
O	-11.472979	-12.677463	6.928321
C	-11.796280	-12.992597	8.273915
H	-12.240140	-12.138772	8.791684
H	-10.914348	-13.308371	8.836175
H	-12.516998	-13.810448	8.224365
H	-8.697471	-9.620119	6.848654
H	-7.176491	-7.932415	6.317061
C	-4.058227	-4.467813	2.889670
C	-3.170114	-3.478569	2.570216
C	-2.402983	-2.617868	3.427607
H	-3.012438	-3.312149	1.513599
H	-4.505973	-4.976888	2.041526
H	-4.508652	-4.920553	6.278922
H	-3.015788	-3.242251	6.764453
C	-1.192668	-1.235873	6.635900
O	-1.651460	-1.720858	7.660329
O	-0.246829	-0.195414	6.766165

C	0.065778	0.168839	8.105633
H	0.498569	-0.668963	8.656176
H	-0.821131	0.509979	8.643299
H	0.791201	0.979380	8.030883
N	0.001531	0.037900	4.096772
H	0.329021	0.373714	3.209714
H	0.326076	0.398862	4.974961
O	-1.647822	-1.814662	0.579586
H	0.517308	-0.808804	-0.437124
H	0.814236	0.856640	0.138964
H	-0.797352	0.375297	-0.466354

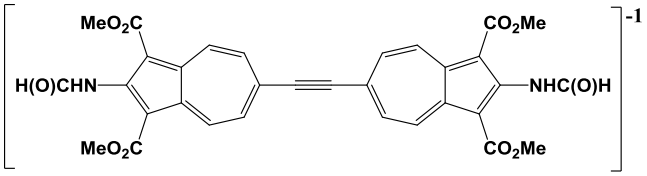
Table A3.20. Cartesian coordinates (Å) for the optimized structure of bis(2-formamido-1,3-dimethoxycarbonyl-6-azulenyl)acetylene (III.2b').



Atom	x	y	z
C	0.054445	-0.064103	0.016896
O	1.320643	0.418169	-0.474077
C	1.369455	0.712501	-1.814443
C	2.681052	1.185559	-2.247138
C	3.821696	1.473493	-1.439461
C	4.898816	1.865088	-2.258827
C	4.437240	1.895816	-3.595744
C	5.206100	2.263689	-4.704395
C	4.863496	2.316499	-6.043297
C	3.642624	2.005881	-6.675663
C	3.597651	2.164857	-8.087970
C	3.562035	2.303914	-9.290718
C	3.511254	2.466865	-10.702344
C	4.681597	2.927585	-11.331950
C	4.933777	3.183335	-12.671817
C	4.099369	3.043355	-13.781717
C	4.448617	3.313034	-15.131387
C	3.305774	3.022993	-15.935192
N	3.316096	3.088839	-17.319006
C	2.677138	2.243269	-18.202254
H	2.968413	2.477215	-19.240183
O	1.912684	1.351198	-17.925231
H	4.100015	3.605727	-17.699193
C	2.234525	2.621847	-15.112716
C	2.702313	2.587420	-13.778148
C	1.940220	2.210744	-12.667752
C	2.288895	2.153688	-11.330660
H	1.506493	1.815015	-10.662311
H	0.930887	1.894813	-12.900227
C	0.824519	2.400871	-15.489116
O	0.071887	1.628259	-14.935920
O	0.427325	3.235588	-16.471067
C	-0.909844	3.029738	-16.961292

H	-1.007367	2.024791	-17.369292
H	-1.048175	3.774771	-17.739954
H	-1.637072	3.170675	-16.162915
C	5.755471	3.795607	-15.567784
O	6.733020	3.956515	-14.867676
O	5.797488	4.093274	-16.907683
C	7.058319	4.586106	-17.402006
H	7.845989	3.853159	-17.235493
H	7.323286	5.518032	-16.905012
H	6.907447	4.750819	-18.465383
H	5.929938	3.539932	-12.897151
H	5.513797	3.115437	-10.664044
C	2.467568	1.552528	-6.049381
C	2.208253	1.304240	-4.709524
C	3.038073	1.446384	-3.596455
H	1.209438	0.953321	-4.486958
H	1.637638	1.365190	-6.720239
H	5.650301	2.649005	-6.709597
H	6.215894	2.575849	-4.468902
C	6.307962	2.081288	-1.876646
O	7.067138	2.846964	-2.430576
O	6.696142	1.250753	-0.887557
C	8.031872	1.453061	-0.392020
H	8.133154	2.460748	0.008225
H	8.762427	1.301456	-1.185412
H	8.161934	0.713592	0.393349
N	3.804985	1.414183	-0.055300
H	3.017593	0.901924	0.323928
C	4.443126	2.262077	0.826291
H	4.146880	2.034431	1.864210
O	5.212119	3.149812	0.547829
O	0.393317	0.556851	-2.517701
H	-0.727416	0.673697	-0.155507
H	0.199843	-0.225990	1.081471
H	-0.214993	-0.996004	-0.477735

Table A3.21. Cartesian coordinates (Å) for the optimized structure of [bis(2-formamido-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-1}$ (III.2b'$^{-1}$).

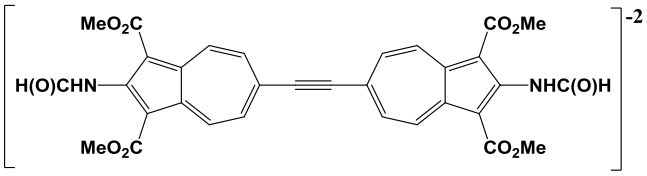


Atom	x	y	z
C	0.00000000	0.00000000	0.00000000
O	1.29542424	0.33727945	-0.51183810
C	1.33103957	0.71145141	-1.84910823
C	2.67797632	0.94525312	-2.33195409
C	3.86019835	1.13628088	-1.56126847
C	4.95765227	1.28995822	-2.42400830
C	4.47158873	1.22583738	-3.76480280
C	5.27871702	1.32109384	-4.92628165

C	4.92827908	1.25085338	-6.24935087
C	3.65114068	1.06002899	-6.86102014
C	3.59946812	1.08986003	-8.25332975
C	3.56344384	1.16272914	-9.47643693
C	3.53424757	1.32913662	-10.8597284
C	4.74634153	1.73761755	-11.4920426
C	4.99014304	2.11233613	-12.7880977
C	4.11164623	2.17860100	-13.8965437
C	4.45127442	2.68073881	-15.1907128
C	3.28885750	2.57660927	-16.0062362
N	3.27085978	2.92995006	-17.3624067
C	2.72743545	2.22562959	-18.3990719
H	2.97133210	2.71193436	-19.3626027
O	2.06734868	1.21010107	-18.3386026
H	3.97949421	3.60518694	-17.6173110
C	2.23733826	2.02891094	-15.2516710
C	2.73399853	1.76911833	-13.9368404
C	1.96146013	1.27425164	-12.8551968
C	2.29713349	1.10276399	-11.5368959
H	1.50038171	0.73949161	-10.8970719
H	0.94690005	1.00241606	-13.1169017
C	0.83928281	1.84081491	-15.6512014
O	0.07685124	1.01126077	-15.1957333
O	0.42529385	2.76508416	-16.5605088
C	-0.91917015	2.60716530	-17.0278200
H	-1.07285940	1.60715664	-17.4325412
H	-1.04771678	3.35424524	-17.8075332
H	-1.63140144	2.78144651	-16.2198510
C	5.74629031	3.22748708	-15.5450826
O	6.78112804	3.14459069	-14.9109694
O	5.72781374	3.94697895	-16.7328143
C	6.96405515	4.58602691	-17.0796756
H	7.75497856	3.85065295	-17.2240301
H	7.26967787	5.28367306	-16.3003327
H	6.76837120	5.12095421	-18.0067681
H	6.00292421	2.42721465	-12.9999417
H	5.59775412	1.80083092	-10.8234184
C	2.42715741	0.86073490	-6.15488716
C	2.17174165	0.83117143	-4.80734186
C	3.05249837	1.00048727	-3.71094351
H	1.13779613	0.67043385	-4.53205425
H	1.56359737	0.71465650	-6.79441395
H	5.74434505	1.36932963	-6.95363192
H	6.32746054	1.50415972	-4.72981895
C	6.37263562	1.40960796	-2.06218846
O	7.22837252	1.96713694	-2.72030736
O	6.67088232	0.74966281	-0.91005122
C	8.00540877	0.93468807	-0.42139601
H	8.18030146	1.98480239	-0.18691966
H	8.73914392	0.60025269	-1.15506049
H	8.07180448	0.33035270	0.48011264

N	3.85808573	1.23640847	-0.16364437
H	3.06833973	0.78318392	0.27681060
C	4.52413368	2.14515113	0.60841314
H	4.21584712	2.04725652	1.66661849
O	5.34094415	2.96752364	0.24937250
O	0.29459282	0.77692448	-2.48242729
H	-0.65924178	0.86822664	0.00105231
H	0.16855329	-0.35354080	1.01515655
H	-0.45778639	-0.78625255	-0.59942139

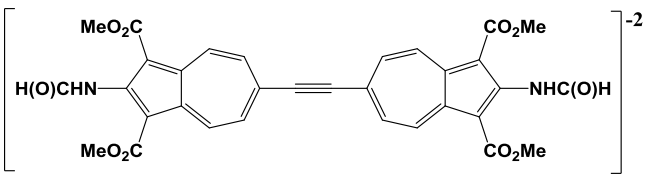
Table A3.22. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [bis(2-formamido-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-2}$ (III.2b'$^{-2}$).



Atom	x	y	z
C	0.124949	-0.079419	0.060817
O	1.398046	0.338014	-0.423722
C	1.414368	0.787076	-1.758824
C	2.711600	1.233456	-2.190178
C	3.876227	1.435867	-1.389653
C	4.931358	1.837694	-2.220850
C	4.427719	1.920588	-3.568116
C	5.221408	2.278159	-4.716564
C	4.887120	2.332181	-6.032158
C	3.635669	2.049987	-6.709218
C	3.586775	2.179618	-8.069188
C	3.542150	2.299040	-9.306454
C	3.493480	2.432198	-10.666091
C	4.694922	2.848072	-11.362482
C	4.934481	3.070588	-12.682173
C	4.057248	2.955500	-13.818660
C	4.419851	3.258912	-15.182761
C	3.255405	3.059378	-15.984201
N	3.251822	3.191653	-17.388144
C	2.706168	2.382549	-18.330399
H	3.004771	2.727924	-19.341934
O	1.981165	1.414617	-18.181062
H	3.981145	3.803042	-17.728897
C	2.199708	2.656050	-15.154448
C	2.702744	2.569597	-13.807177
C	1.908264	2.210188	-12.659845
C	2.242006	2.152824	-11.344245
H	1.445698	1.845923	-10.673201
H	0.889232	1.931242	-12.895391
C	0.810587	2.442270	-15.539154
O	0.005278	1.704365	-15.000832
O	0.430015	3.238361	-16.590693
C	-0.858229	2.955886	-17.131047
H	-0.907907	1.926545	-17.488338

H	-0.984459	3.647252	-17.963497
H	-1.642709	3.113124	-16.388467
C	5.717506	3.705534	-15.612616
O	6.758968	3.755025	-14.979386
O	5.734767	4.156478	-16.947049
C	7.008577	4.572697	-17.430740
H	7.733285	3.757542	-17.391291
H	7.399832	5.408670	-16.848651
H	6.846466	4.879786	-18.463835
H	5.941769	3.378847	-12.927127
H	5.541336	3.010955	-10.702214
C	2.434793	1.634985	-6.011376
C	2.195847	1.415603	-4.691036
C	3.073466	1.533856	-3.555161
H	1.188804	1.107455	-4.444933
H	1.588192	1.470033	-6.670901
H	5.682826	2.638440	-6.704200
H	6.240208	2.558781	-4.482021
C	6.320678	2.052628	-1.837415
O	7.125360	2.789985	-2.377426
O	6.701866	1.259334	-0.783995
C	7.990208	1.543593	-0.244792
H	8.039724	2.573880	0.109765
H	8.774485	1.384604	-0.987220
H	8.116896	0.854438	0.589419
N	3.880455	1.307189	0.014614
H	3.151361	0.696562	0.357207
C	4.425874	2.119097	0.954630
H	4.126856	1.776802	1.967093
O	5.149263	3.087816	0.802590
O	0.373281	0.733251	-2.392322
H	-0.601070	0.734499	0.019946
H	0.287641	-0.384347	1.094459
H	-0.264994	-0.917101	-0.519692

Table A3.23. Cartesian coordinates (Å) for the triplet state (T) optimized structure of [bis(2-formamido-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-2}$ (III.2b'$^{-2}$).

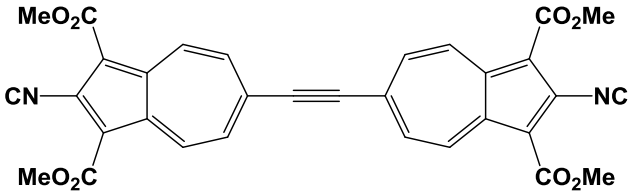


Atom	x	y	z
C	0.269703	3.021667	0.302815
O	1.439564	2.428909	-0.252493
C	1.677958	2.724819	-1.609010
C	2.888441	2.132443	-2.112480
C	3.910526	1.465549	-1.367607
C	4.891514	1.007433	-2.260936
C	4.509330	1.410229	-3.587971
C	5.256410	1.106584	-4.781467
C	4.959673	1.379221	-6.088806

C	3.836918	2.042230	-6.680199
C	3.804560	2.170074	-8.094297
C	3.758343	2.290174	-9.310249
C	3.696670	2.442415	-10.720946
C	4.279955	3.612488	-11.291998
C	4.350856	4.049182	-12.590542
C	3.840373	3.439652	-13.787954
C	3.916114	4.013854	-15.107331
C	3.250225	3.119539	-16.001701
N	3.193083	3.321752	-17.394807
C	3.377118	2.437496	-18.407761
H	3.374615	2.972835	-19.379757
O	3.521828	1.228656	-18.351738
H	3.295073	4.292762	-17.657080
C	2.766610	2.026101	-15.266411
C	3.148978	2.208210	-13.892154
C	2.812430	1.303565	-12.822942
C	3.048578	1.415331	-11.480062
H	2.684003	0.589040	-10.877143
H	2.306750	0.401014	-13.139551
C	1.937435	0.934050	-15.759562
O	1.880234	-0.199235	-15.319603
O	1.119799	1.324207	-16.790440
C	0.413627	0.268101	-17.437387
H	1.110324	-0.464022	-17.847628
H	-0.147969	0.740905	-18.242006
H	-0.266715	-0.234104	-16.746936
C	4.528507	5.276259	-15.423310
O	5.224827	5.986666	-14.718203
O	4.239019	5.720459	-16.728181
C	4.856266	6.948960	-17.101971
H	5.944364	6.877414	-17.050221
H	4.534777	7.766566	-16.454851
H	4.541924	7.138396	-18.128024
H	4.862158	4.989030	-12.743572
H	4.742093	4.270754	-10.562331
C	2.745810	2.584597	-5.937703
C	2.489236	2.610607	-4.590194
C	3.267760	2.085483	-3.502037
H	1.570749	3.098125	-4.295667
H	1.988011	3.055850	-6.556519
H	5.697584	1.040054	-6.809611
H	6.196023	0.599576	-4.607145
C	6.050296	0.181428	-1.945878
O	7.105542	0.135601	-2.550708
O	5.823362	-0.648839	-0.876671
C	6.966227	-1.356639	-0.403319
H	7.745363	-0.661073	-0.088921
H	7.368333	-2.019097	-1.172160
H	6.618404	-1.937727	0.449901
N	3.909481	1.381392	0.038336

H	2.984361	1.467424	0.437075
C	4.924787	1.562782	0.920847
H	4.530668	1.535528	1.957590
O	6.111953	1.728273	0.699748
O	0.856559	3.407231	-2.198084
H	0.315313	4.111313	0.252044
H	0.238721	2.697262	1.342810
H	-0.628813	2.690457	-0.219847

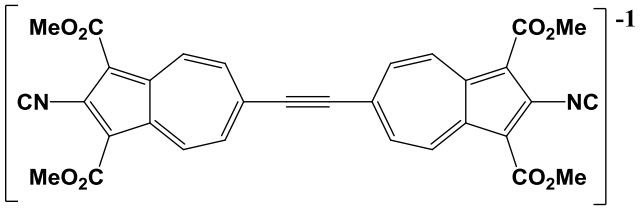
Table A3.24. Cartesian coordinates (Å) for the optimized structure of bis(2-isocyano-1,3-dimethoxycarbonyl-6-azulenyl)acetylene (III.2c').



Atom	x	y	z
C	0.079297	-0.069350	0.032071
O	-0.267292	-0.427610	1.382351
C	-1.200734	-1.383396	1.526784
C	-1.497214	-1.684399	2.938702
C	-0.955412	-1.071361	4.094938
C	-1.501322	-1.648039	5.267916
C	-2.411125	-2.653740	4.851907
C	-3.163972	-3.468884	5.702283
C	-4.068180	-4.473129	5.400556
C	-4.490526	-4.961359	4.149524
C	-5.441939	-6.018399	4.164586
C	-6.255440	-6.914973	4.177831
C	-7.206174	-7.972626	4.192934
C	-7.628578	-8.425377	5.457174
C	-8.533081	-9.420474	5.787003
C	-9.285385	-10.259781	4.959923
C	-10.196615	-11.252145	5.404016
C	-10.739794	-11.864001	4.247786
N	-11.657414	-12.871869	4.262084
C	-12.459485	-13.726398	4.274400
C	-10.195074	-11.286301	3.074757
C	-9.285140	-10.280690	3.490709
C	-8.533396	-9.464593	2.640263
C	-7.629416	-8.460122	2.941918
H	-7.178718	-7.973291	2.085574
H	-8.689492	-9.653645	1.586302
C	-10.486013	-11.631885	1.671887
O	-9.975112	-11.095455	0.707557
O	-11.390746	-12.618525	1.554963
C	-11.734220	-13.017968	0.215535
H	-12.165286	-12.181257	-0.332970
H	-12.462483	-13.814305	0.336004
H	-10.852422	-13.378579	-0.312772
C	-10.491146	-11.554800	6.815995
O	-9.963162	-11.007751	7.765005
O	-11.420183	-12.514837	6.960619

C	-11.765342	-12.874222	8.310964
H	-12.178850	-12.016095	8.839563
H	-10.888193	-13.237390	8.845177
H	-12.508543	-13.659761	8.213229
H	-8.688104	-9.580602	6.845906
H	-7.177072	-7.915310	6.299521
C	-4.066616	-4.509901	2.885324
C	-3.161189	-3.515622	2.555571
C	-2.409408	-2.675902	3.382707
H	-3.005132	-3.356362	1.496687
H	-4.517586	-5.020406	2.042956
H	-4.519964	-4.959034	6.256853
H	-3.008790	-3.279075	6.756244
C	-1.211559	-1.301468	6.670782
O	-1.723133	-1.837363	7.635054
O	-0.305814	-0.315775	6.787802
C	0.037080	0.084112	8.127245
H	0.471121	-0.751574	8.674996
H	-0.845503	0.441631	8.656307
H	0.762871	0.882707	8.006790
N	-0.038178	-0.063158	4.080655
C	0.758598	0.796305	4.068294
O	-1.730412	-1.928631	0.577678
H	0.485812	-0.929908	-0.497982
H	0.828369	0.710572	0.129959
H	-0.795667	0.301042	-0.500784

Table A3.25. Cartesian coordinates (Å) for the optimized structure of [bis(2-isocyano-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-1}$ (III.2c'$^{-1}$).

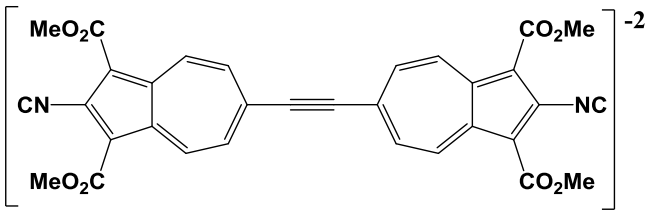


Atom	x	y	z
C	0.086646	-0.064462	0.042405
O	-0.245991	-0.415165	1.389674
C	-1.196969	-1.370823	1.540666
C	-1.488405	-1.669498	2.943375
C	-0.937830	-1.051546	4.094741
C	-1.489925	-1.635504	5.263122
C	-2.404517	-2.644280	4.837053
C	-3.168346	-3.472205	5.700455
C	-4.064439	-4.467197	5.407816
C	-4.506160	-4.976019	4.149929
C	-5.437618	-6.012658	4.164677
C	-6.259515	-6.920930	4.178012
C	-7.190426	-7.958059	4.192779
C	-7.631888	-8.431494	5.464455
C	-8.527817	-9.418013	5.784878
C	-9.291190	-10.270358	4.945114
C	-10.206904	-11.265780	5.399338

C	-10.757468	-11.883720	4.247955
N	-11.676851	-12.896067	4.262383
C	-12.475430	-13.751834	4.274417
C	-10.205346	-11.299763	3.079585
C	-9.291057	-10.290718	3.505671
C	-8.527316	-9.462708	2.642272
C	-7.631657	-8.467325	2.934902
H	-7.181440	-7.982499	2.075958
H	-8.684787	-9.654280	1.589939
C	-10.492837	-11.641366	1.685841
O	-9.992107	-11.119393	0.705002
O	-11.406531	-12.636565	1.562769
C	-11.739009	-13.025644	0.226106
H	-12.167661	-12.189092	-0.326880
H	-12.468813	-13.823896	0.334680
H	-10.856692	-13.384065	-0.305250
C	-10.497904	-11.564866	6.802051
O	-9.976323	-11.035527	7.767912
O	-11.444191	-12.525169	6.953067
C	-11.776522	-12.876059	8.300362
H	-12.174229	-12.015320	8.839183
H	-10.900897	-13.250417	8.831774
H	-12.531313	-13.653533	8.214602
H	-8.684410	-9.580643	6.842207
H	-7.181769	-7.922615	6.309492
C	-4.064673	-4.502614	2.878249
C	-3.168284	-3.516515	2.557831
C	-2.404528	-2.664526	3.397604
H	-3.011850	-3.353738	1.500498
H	-4.515159	-5.011165	2.033212
H	-4.514690	-4.951997	6.266758
H	-3.010628	-3.280855	6.752792
C	-1.202183	-1.294080	6.656852
O	-1.702515	-1.816372	7.637723
O	-0.287358	-0.299909	6.779896
C	0.045781	0.088625	8.116554
H	0.475289	-0.748009	8.668770
H	-0.836364	0.446239	8.648716
H	0.775114	0.887303	8.007939
N	-0.018815	-0.038877	4.080243
C	0.775008	0.821298	4.067909
O	-1.721015	-1.897723	0.574809
H	0.478406	-0.926831	-0.498155
H	0.846155	0.708401	0.128191
H	-0.787440	0.315917	-0.487269

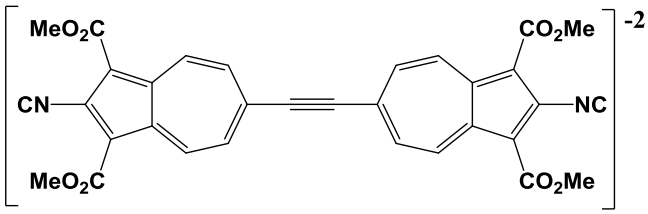
Table A3.26. Cartesian coordinates (Å) for the singlet state (S) optimized structure of [bis(2-isocyano-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-2}$ (III.2c'$^{-2}$).

Atom	x	y	z
C	0.106936	-0.054927	0.051325
O	-0.211592	-0.399918	1.395357
C	-1.183318	-1.354098	1.552860
C	-1.472322	-1.648712	2.947109
C	-0.913866	-1.023210	4.094406
C	-1.474821	-1.613749	5.259058
C	-2.394960	-2.625963	4.824604
C	-3.171387	-3.467115	5.701434
C	-4.059277	-4.454786	5.416028
C	-4.519708	-4.987737	4.150308
C	-5.431945	-6.005757	4.164753
C	-6.264497	-6.928484	4.178087
C	-7.176220	-7.946964	4.192519
C	-7.636576	-8.444109	5.472717
C	-8.524272	-9.423515	5.785690
C	-9.300168	-10.289527	4.932861
C	-10.221683	-11.287845	5.395605
C	-10.781359	-11.912157	4.248246
N	-11.699720	-12.928209	4.262890
C	-12.495543	-13.786569	4.275129
C	-10.221355	-11.320670	3.083619
C	-9.300918	-10.308754	3.518136
C	-8.525178	-9.466945	2.641338
C	-7.637318	-8.479265	2.926777
H	-7.188143	-7.995796	2.064862
H	-8.684396	-9.661280	1.590109
C	-10.506361	-11.658181	1.698254
O	-10.014461	-11.151818	0.701332
O	-11.435460	-12.657954	1.568964
C	-11.758758	-13.036217	0.235133
H	-12.179790	-12.197803	-0.323761
H	-12.494947	-13.832109	0.332160
H	-10.877771	-13.398481	-0.298808
C	-10.508909	-11.584142	6.789866
O	-9.990200	-11.075864	7.772053
O	-11.475703	-12.543321	6.947460
C	-11.793625	-12.888626	8.291556
H	-12.175235	-12.026521	8.842674
H	-10.919024	-13.275002	8.819024
H	-12.559799	-13.658195	8.217410
H	-8.681555	-9.589950	6.841994
H	-7.186887	-7.937076	6.320779
C	-4.058247	-4.491647	2.870097
C	-3.169997	-3.512757	2.557092
C	-2.394682	-2.646204	3.409888
H	-3.011905	-3.347087	1.500781
H	-4.507388	-4.999215	2.022063
H	-4.509192	-4.937562	6.277948
H	-3.012878	-3.272091	6.752646



C	-1.190850	-1.275165	6.644368
O	-1.684360	-1.779929	7.641305
O	-0.260784	-0.276270	6.773573
C	0.061185	0.103380	8.107334
H	0.481981	-0.734379	8.667406
H	-0.820385	0.465872	8.640139
H	0.797252	0.899373	8.010212
N	0.003719	-0.006473	4.079610
C	0.794702	0.856342	4.066992
O	-1.704209	-1.860098	0.570657
H	0.482755	-0.918631	-0.501260
H	0.877703	0.710036	0.125538
H	-0.765924	0.337323	-0.474693

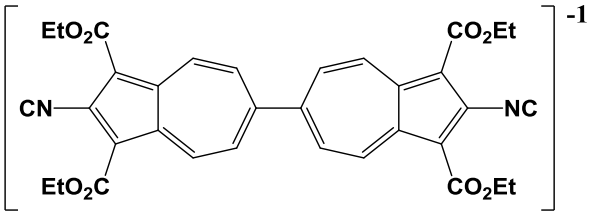
Table A3.27. Cartesian coordinates (Å) for the triplet state (T) optimized structure of bis(2-isocyano-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-2}$ (III.2c'$^{-2}$).



Atom	x	y	z
C	0.113319	-0.039182	0.047165
O	-0.205968	-0.381780	1.391387
C	-1.173053	-1.340350	1.549893
C	-1.459901	-1.632552	2.944653
C	-0.896379	-1.003739	4.094077
C	-1.459876	-1.599765	5.261004
C	-2.378264	-2.608753	4.831224
C	-3.151266	-3.446661	5.704561
C	-4.046217	-4.442501	5.400956
C	-4.489857	-4.954076	4.149961
C	-5.440770	-6.014945	4.165054
C	-6.256350	-6.918655	4.178186
C	-7.206745	-7.979991	4.193197
C	-7.649857	-8.456601	5.458097
C	-8.544436	-9.443817	5.789492
C	-9.317301	-10.306157	4.940061
C	-10.236805	-11.301642	5.398025
C	-10.799186	-11.931308	4.248495
N	-11.713681	-12.944704	4.263001
C	-12.510321	-13.805017	4.275168
C	-10.234464	-11.336198	3.081689
C	-9.316887	-10.326542	3.511634
C	-8.543395	-9.488948	2.638425
C	-7.649231	-8.492445	2.942150
H	-7.198584	-8.007302	2.081660
H	-8.696833	-9.678214	1.586286
C	-10.516954	-11.671604	1.695731
O	-10.021768	-11.165693	0.699896
O	-11.444030	-12.672983	1.565447
C	-11.764895	-13.052107	0.231516

H	-12.186821	-12.214659	-0.328244
H	-12.499736	-13.849363	0.327599
H	-10.882633	-13.412882	-0.301430
C	-10.524569	-11.593210	6.792729
O	-10.009637	-11.078786	7.774014
O	-11.486524	-12.556963	6.951057
C	-11.807503	-12.897969	8.295279
H	-12.195895	-12.035571	8.841276
H	-10.932841	-13.277226	8.827889
H	-12.569227	-13.672026	8.221948
H	-8.697262	-9.604067	6.846533
H	-7.199553	-7.947237	6.304729
C	-4.047493	-4.476965	2.884980
C	-3.152974	-3.489752	2.553450
C	-2.379281	-2.628055	3.402778
H	-3.001165	-3.328721	1.496376
H	-4.498615	-4.985713	2.038414
H	-4.496406	-4.927946	6.261518
H	-2.996840	-3.258140	6.756691
C	-1.175578	-1.265738	6.646914
O	-1.669314	-1.772767	7.642896
O	-0.246281	-0.266390	6.776998
C	0.076878	0.110928	8.110888
H	0.499012	-0.727508	8.669034
H	-0.804293	0.471748	8.645581
H	0.812228	0.907693	8.014637
N	0.017449	0.010244	4.079341
C	0.809274	0.874983	4.066695
O	-1.692280	-1.850666	0.568732
H	0.494590	-0.902543	-0.502306
H	0.880097	0.729879	0.120374
H	-0.760449	0.347122	-0.481847

Table A3.28. Cartesian coordinates (Å) for the optimized structure of [2,2'-diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl]$^{-1}$ (III.1c^{-1}).

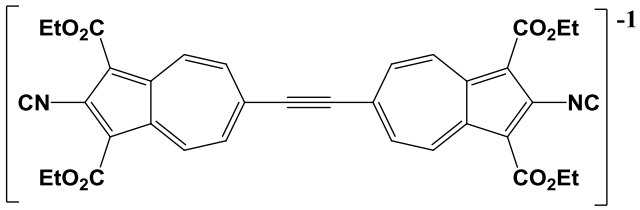


Atom	x	y	z
C	-0.007985	-0.015302	-0.060353
O	-0.654289	-0.068790	1.235786
C	-1.385706	-1.201007	1.485367
C	-1.960080	-1.215592	2.834189
C	-1.628283	-0.375512	3.940653
N	-0.680787	0.609373	3.924951
C	0.140957	1.462271	3.909840
C	-2.436851	-0.722734	5.065843
C	-3.292013	-1.795676	4.655349
C	-4.256840	-2.437524	5.477337
H	-4.339477	-2.012327	6.479034

C	-5.114878	-3.484355	5.195886
H	-5.783457	-3.736339	6.021958
C	-5.325246	-4.243666	4.004506
C	-4.600843	-4.015749	2.794827
H	-4.836475	-4.708126	1.983730
C	-3.601408	-3.113612	2.480553
H	-3.191330	-3.192234	1.472297
C	-2.988235	-2.109038	3.276483
C	-6.333658	-5.310517	4.025042
C	-6.543554	-6.022604	5.245321
C	-7.397786	-7.060734	5.566443
C	-8.358925	-7.737695	4.768802
C	-9.184618	-8.820354	5.210818
C	-9.985552	-9.220139	4.098363
N	-10.960067	-10.178016	4.136607
C	-11.811350	-11.000718	4.173317
C	-9.674060	-8.406921	2.966093
C	-8.657060	-7.485393	3.376142
C	-8.047880	-6.509229	2.542821
C	-7.055167	-5.588713	2.824129
H	-6.821442	-4.927659	1.986709
H	-8.454413	-6.474682	1.530747
C	-10.262747	-8.463734	1.624681
O	-10.122424	-7.620418	0.740107
O	-11.009740	-9.595903	1.424693
C	-11.667046	-9.691540	0.136683
H	-12.334176	-8.825090	0.010064
C	-12.431509	-11.002745	0.115590
H	-11.750776	-11.857649	0.225166
H	-13.164545	-11.044140	0.932312
H	-12.965341	-11.104412	-0.841347
H	-10.909255	-9.640892	-0.660281
C	-9.181189	-9.379495	6.565830
O	-8.675602	-8.859180	7.559126
O	-9.803757	-10.599132	6.631573
C	-9.887258	-11.189222	7.952872
H	-10.458755	-10.515761	8.610013
H	-8.874464	-11.276623	8.374173
C	-10.561830	-12.541259	7.801317
H	-9.971001	-13.203813	7.154150
H	-10.661063	-13.017279	8.788344
H	-11.561434	-12.435854	7.360082
H	-7.331957	-7.428200	6.591989
H	-5.878246	-5.734053	6.061898
C	-2.425150	-0.125927	6.404953
O	-3.278120	-0.293768	7.275302
O	-1.328204	0.667877	6.618995
C	-1.281111	1.336386	7.903861
H	-1.333025	0.583401	8.705159
H	-2.166793	1.982816	8.003335
C	0.009391	2.134136	7.951222

H	0.883601	1.474278	7.869726
H	0.053395	2.860602	7.128785
H	0.073088	2.678686	8.905343
O	-1.523248	-2.079324	0.635132
H	0.667384	-0.878984	-0.159438
C	0.741423	1.302527	-0.138063
H	1.481850	1.383261	0.668915
H	1.264558	1.373994	-1.103581
H	0.051903	2.153299	-0.053846
H	-0.771623	-0.103918	-0.848291

Table A3.29. Cartesian coordinates (Å) for the optimized structure of [bis(2-isocyano-1,3-dimethoxycarbonyl-6-azulenyl)acetylene]$^{-1}$ (III.2c^{-1}).



Atom	x	y	z
C	0.084485	-0.073483	-0.031510
O	-0.246155	-0.441623	1.331153
C	-1.389530	-1.180327	1.483642
C	-1.685788	-1.472108	2.890615
C	-1.120284	-0.861025	4.049713
C	-1.692311	-1.436584	5.223938
C	-2.631071	-2.428202	4.794033
C	-3.401083	-3.251079	5.661159
C	-4.312649	-4.242442	5.363592
C	-4.755892	-4.747291	4.097966
C	-5.698235	-5.780630	4.111262
C	-6.528275	-6.696076	4.124007
C	-7.463397	-7.735872	4.140276
C	-7.906330	-8.204984	5.419661
C	-8.802488	-9.201474	5.745685
C	-9.560144	-10.060431	4.902797
C	-10.456870	-11.078133	5.361641
C	-10.992506	-11.720069	4.204603
N	-11.941756	-12.703679	4.218665
C	-12.771179	-13.548972	4.229626
C	-10.448345	-11.122579	3.028221
C	-9.555856	-10.087227	3.454093
C	-8.794776	-9.259419	2.583639
C	-7.900770	-8.250923	2.876755
H	-7.446057	-7.760827	2.012395
H	-8.962871	-9.454578	1.523249
C	-10.728224	-11.468533	1.630236
O	-10.424114	-10.794566	0.647103
O	-11.372409	-12.670756	1.505409
C	-11.721914	-13.056244	0.152261
H	-12.358945	-12.274869	-0.289623

C	-12.436752	-14.393368	0.233400
H	-11.783552	-15.163726	0.665209
H	-13.337215	-14.320552	0.856920
H	-12.733388	-14.715610	-0.775622
H	-10.804996	-13.113426	-0.453840
C	-10.747779	-11.369352	6.769707
O	-10.433604	-10.667794	7.730151
O	-11.418765	-12.552168	6.934190
C	-11.775730	-12.884507	8.299342
H	-12.391618	-12.073112	8.716262
H	-10.859500	-12.945511	8.906180
C	-12.524681	-14.204768	8.262450
H	-11.892997	-15.004841	7.853398
H	-12.826128	-14.487350	9.281867
H	-13.425042	-14.128908	7.639252
H	-8.974490	-9.358046	6.811886
H	-7.455019	-7.684052	6.267626
C	-4.306048	-4.280244	2.820202
C	-3.392878	-3.297977	2.498419
C	-2.627461	-2.449700	3.344999
H	-3.232956	-3.126614	1.432517
H	-4.763448	-4.792690	1.970358
H	-4.774558	-4.729562	6.225804
H	-3.245984	-3.048846	6.722247
C	-1.404035	-1.102579	6.623069
O	-2.066141	-1.453270	7.598551
O	-0.272628	-0.342244	6.758631
C	0.051762	0.060887	8.112839
H	0.175584	-0.838119	8.735726
H	-0.792084	0.633276	8.527593
C	1.321527	0.890120	8.045944
H	2.155651	0.301430	7.640694
H	1.182562	1.770679	7.405421
H	1.595152	1.229760	9.055662
N	-0.229140	0.175690	4.035753
C	0.540439	1.075790	4.022667
O	-2.054783	-1.547173	0.516372
H	0.199511	-0.987731	-0.633514
C	1.363333	0.743181	0.018620
H	2.190660	0.154238	0.437247
H	1.641367	1.057975	-0.997919
H	1.233386	1.638692	0.639901
H	-0.752439	0.498459	-0.460610

Table A3.30. TD-DFT analysis of the electronic spectrum of III.1c.

Calc. Transition (nm)	Oscillator Strength	Composition (%)
514	0.010893153	91% HOMO→LUMO
		4% HOMO-1→LUMO+1
		3% HOMO-2→LUMO+2
		1% HOMO-3→LUMO+3

	0.002739574	91% HOMO-1→LUMO
		4% HOMO→LUMO+1
		3% HOMO-2→LUMO+3
		1% HOMO-3→LUMO+2
388	0.620559747	84% HOMO-2→LUMO
		10% HOMO→LUMO+1
		3% HOMO-1→LUMO+3

Table A3.31. TD-DFT analysis of the electronic spectrum of III.1c^{-1}.

Calc. Transition (nm)	Oscillator Strength	Composition (%)
763	0.450097361	84% SOMO→LUMO
		12% SOMO-3→SOMO
		1% SOMO→LUMO+2
474	0.000000573	92% SOMO→LUMO+3
		3% SOMO-4→SOMO
		2% SOMO-3→LUMO+1
	0.000691003	93% SOMO-1→SOMO
		3% SOMO-2→LUMO+1
	0.006997501	93% SOMO-2→SOMO
		3% SOMO-1→LUMO+1
		1% SOMO-1→LUMO
	0.018641762	95% SOMO→LUMO+4
		1% SOMO-4→LUMO+1
	1.269119668	69% SOMO-3→SOMO
		9% SOMO→LUMO
		6% SOMO-1→LUMO
		3% SOMO-2→LUMO+2
		3% SOMO-4→LUMO
		2% SOMO-4→LUMO+1
		2% SOMO-2→LUMO+2
		2% SOMO-1→LUMO+1
	0.000063378	22% SOMO-2→LUMO
		16% SOMO-1→LUMO+2
		15% SOMO-4→SOMO
		15% SOMO-2→LUMO+1
		13% SOMO-3→LUMO
		11% SOMO-1→LUMO+2
		4% SOMO-3→LUMO+1
		1% SOMO→LUMO+3
420	0.21317132	30% SOMO-2→LUMO+1
		22% SOMO-1→LUMO

		17% SOMO-2→LUMO+2
		15% SOMO-2→LUMO+2
		11% SOMO-3→SOMO
		2% SOMO→LUMO

Table A3.32. TD-DFT analysis of the electronic spectrum of III.1c^{-2}.

Calc. Transition (nm)	Oscillator Strength	Composition (%)
624	0.699083154	77% HOMO→LUMO
		20% HOMO→LUMO+4
	0.004060196	94% HOMO→LUMO+2
407	2.394961117	72% HOMO→LUMO+4
		18% HOMO→LUMO
		1% HOMO-4→LUMO
		1% HOMO→LUMO+12

Table A3.33. TD-DFT analysis of the electronic spectrum of III.2c.

Calc. Transition (nm)	Oscillator Strength	Composition (%)
540	0.007030655	45.8% HOMO→LUMO
		45.5% HOMO-1→LUMO
		2.1% HOMO→LUMO+1
		2.0% HOMO-1→LUMO+1
		1.4% HOMO-2→LUMO+2
		1.3% HOMO-2→LUMO+3
	0.007985367	46.4% HOMO-1→LUMO
		46.0% HOMO→LUMO
		1.6% HOMO-1→LUMO+1
		1.6% HOMO→LUMO+1
		1.4% HOMO-2→LUMO+2
		1.3% HOMO-2→LUMO+3
426	2.237006184	95.4% HOMO-2→LUMO
	0.001903663	48.5% HOMO→LUMO+1
		40.0% HOMO-1→LUMO+1
		3.2% HOMO-1→LUMO
		2.8% HOMO→LUMO
		2.1% HOMO-2→LUMO+3
		1.9% HOMO-2→LUMO+2
	0.00304454	48.7% HOMO-1→LUMO+1
		40.2% HOMO-1→LUMO+1
		2.6% HOMO→LUMO
		2.4% HOMO-2→LUMO+2
		2.2% HOMO-1→LUMO
		1.8% HOMO-2→LUMO+3
	0.000431156	71.4% HOMO-3→LUMO
		20.1% HOMO-2→LUMO+1

		3.6% HOMO-1→LUMO+2
		3.3% HOMO→LUMO+3

Table A3.34. TD-DFT analysis of the electronic spectrum of III.2c^{-1}.

Calc. Transition (nm)	Oscillator Strength	Composition (%)
832	0.515236173	77.3% SOMO→LUMO
		20.4% SOMO-1→SOMO
	0.00005576	70.8% SOMO→LUMO+1
		26.4% SOMO→LUMO+2
	0.000163612	70.8% SOMO→LUMO+2
		26.4% SOMO→LUMO+1
503	0.003744221	46.7% SOMO-2→SOMO
		44.0% SOMO-3→SOMO
		2.6% SOMO-2→LUMO
		2.6% SOMO-3→LUMO
	0.000029718	87.7% SOMO→LUMO+3
		5.0% SOMO-4→SOMO
		3.4% SOMO-1→LUMO
	0.004583376	47.2% SOMO-3→SOMO
		44.2% SOMO-2→SOMO
		2.2% SOMO-3→LUMO
		2.2% SOMO-2→LUMO
	0.087065135	89.0% SOMO→LUMO+4
		5.0% SOMO-1→SOMO
		1.0% SOMO-10→SOMO
	2.627192877	64.7% SOMO-1→SOMO
		17.0% SOMO→LUMO
		5.0% SOMO-4→LUMO
		4.5% SOMO→LUMO+4

Table A3.35. TD-DFT analysis of the electronic spectrum of III.2c^{-2}.

Calc. Transition (nm)	Oscillator Strength	Composition (%)
605	0.000263994	78.6% HOMO→LUMO+2
		20.7% HOMO→LUMO+3
	0.001327636	78.6% HOMO→LUMO+3
		20.7% HOMO→LUMO+2
	1.023300629	50.0% HOMO→LUMO
		43.6% HOMO→LUMO+4
		4.6% HOMO→LUMO+1
	0.051961274	91.0% HOMO→LUMO+1
		2.5% HOMO→LUMO
		2.3% HOMO→LUMO+4
		1.7% HOMO-1→LUMO

436	4.013620234	47.9% HOMO→LUMO+4
		42.1% HOMO→LUMO
		2.6% HOMO-4→LUMO
	0.014473038	55.7% HOMO-2→LUMO
		31.8% HOMO-3→LUMO
		3.8% HOMO-1→LUMO+2
		3.5% HOMO-1→LUMO+3
		2.1% HOMO-2→LUMO+4
		1.2% HOMO-3→LUMO+3
	0.0151045	55.8% HOMO-3→LUMO
		32.3% HOMO-2→LUMO
		3.6% HOMO-1→LUMO+2
		3.3% HOMO-1→LUMO+3
		2.0% HOMO-3→LUMO+4
		1.2% HOMO-2→LUMO+4

Table A3.36. UV-Vis absorption spectrum of III.1a in CH_2Cl_2 at 24°C.

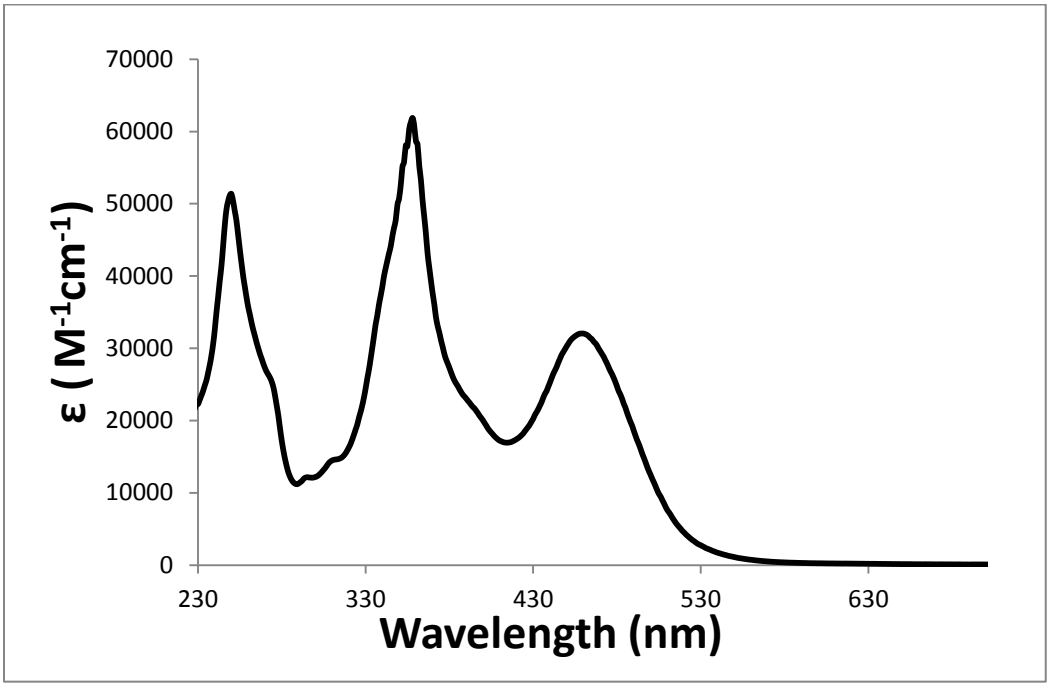


Table A3.37. UV-Vis absorption spectrum of III.1b in CH_2Cl_2 at 24°C.

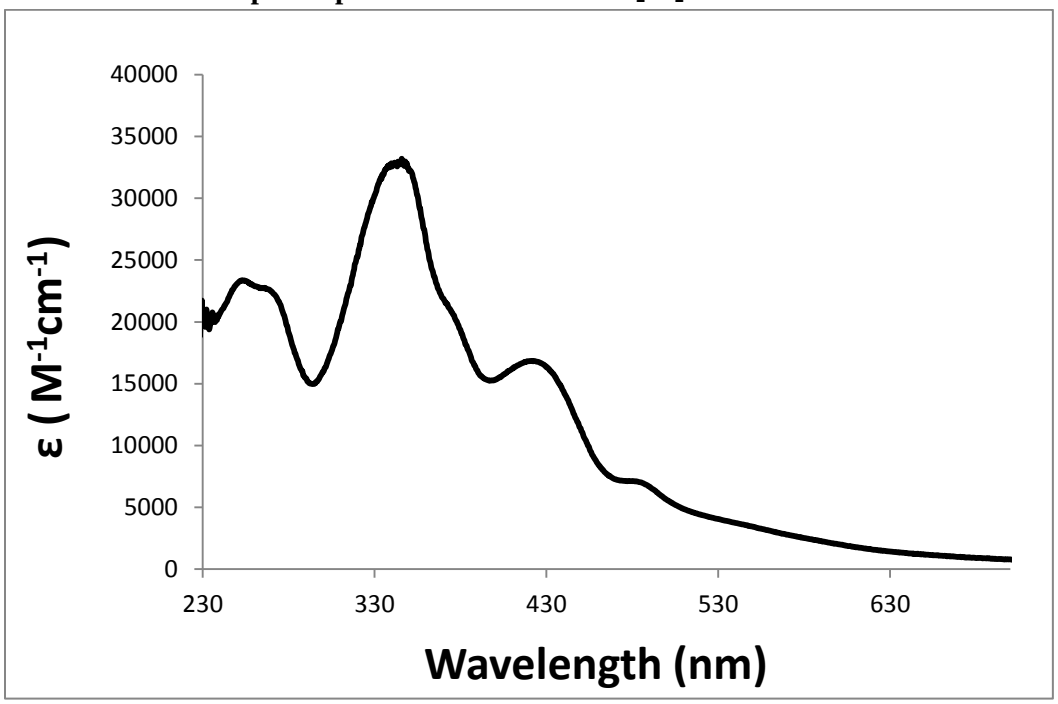


Table A3.38. UV-Vis absorption spectrum of III.1c in CH_2Cl_2 at 24°C.

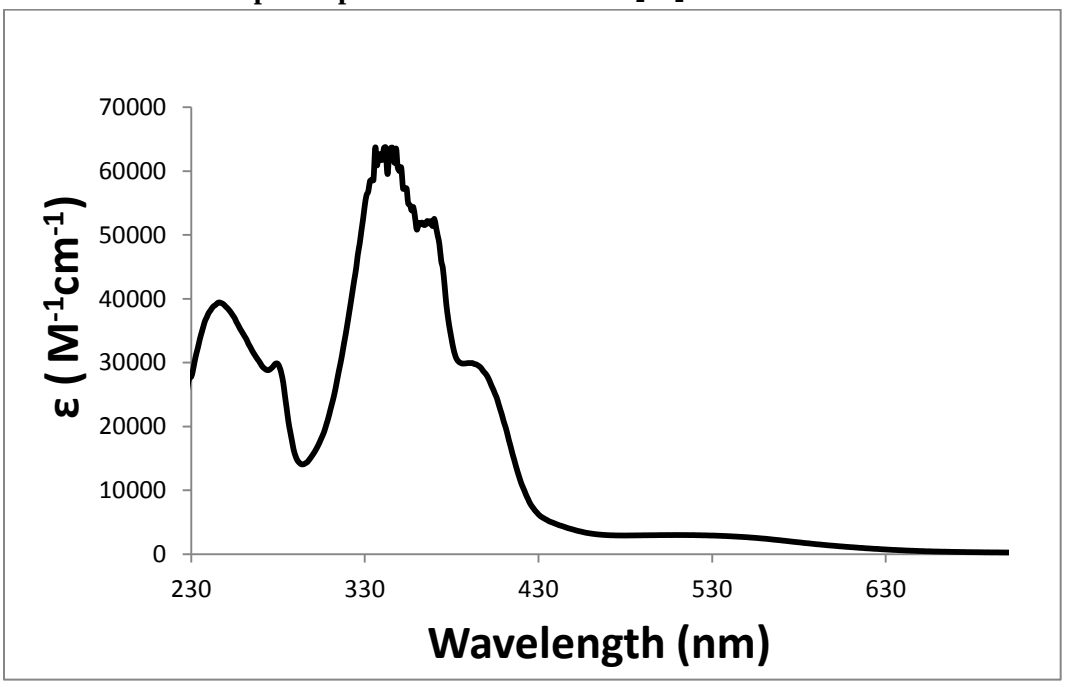


Table A3.39. UV-Vis absorption spectrum of III.1d in CH_2Cl_2 at 24°C.

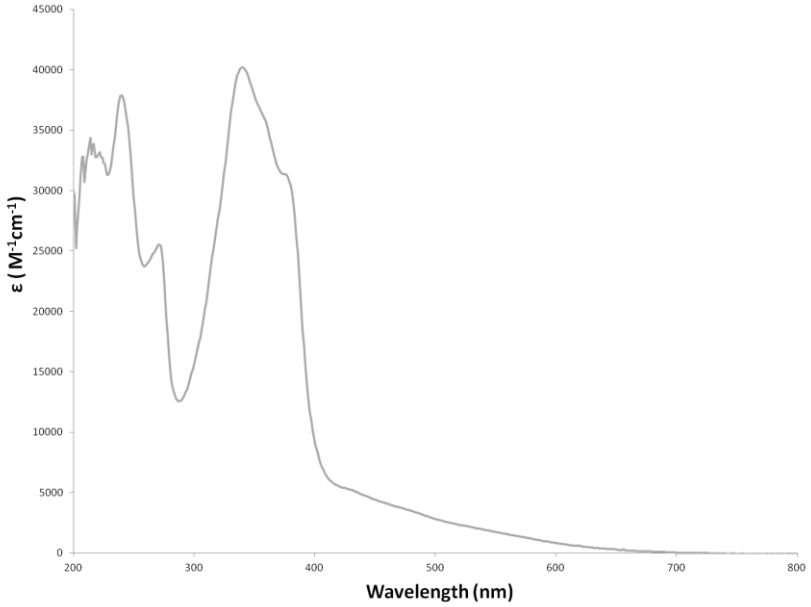


Table A3.40. UV-Vis absorption spectrum of III.2a in CH_2Cl_2 at 24°C.

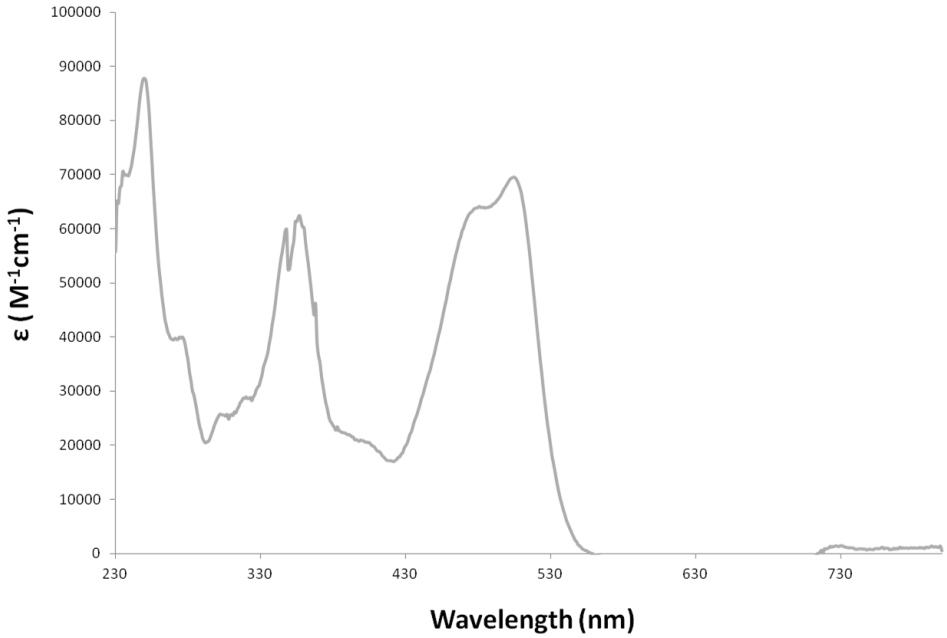


Table A3.41. UV-Vis absorption spectrum of III.2b in CH_2Cl_2 at 24°C.

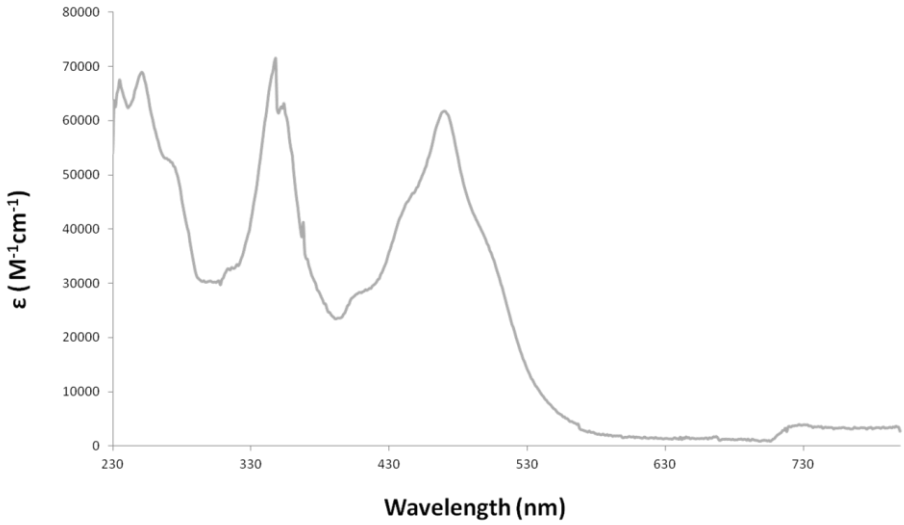
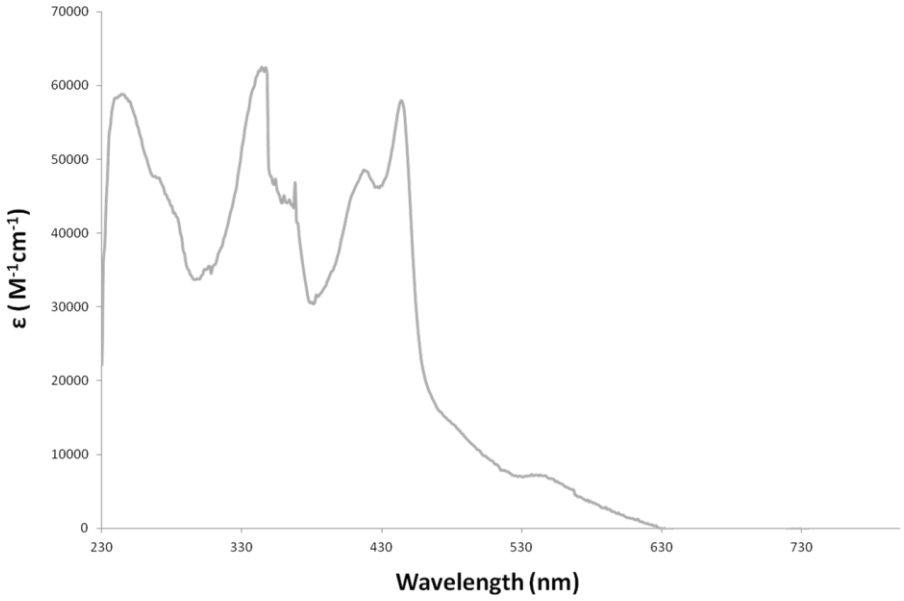


Table A3.42. UV-Vis absorption spectrum of III.2c in CH_2Cl_2 at 24°C.



Appendix 4. X-ray Structure of 2-cyano-1,3-diethoxycarbonylazulene

Synthesis of 2-cyano-1,3-diethoxycarbonyl-azulene was accomplished using a procedure developed by Dr. Kolbe Scheetz.[1] Crystals were grown by slow diffusion of pentane layered over CH_2Cl_2 at -40°C during a period of 3 days.

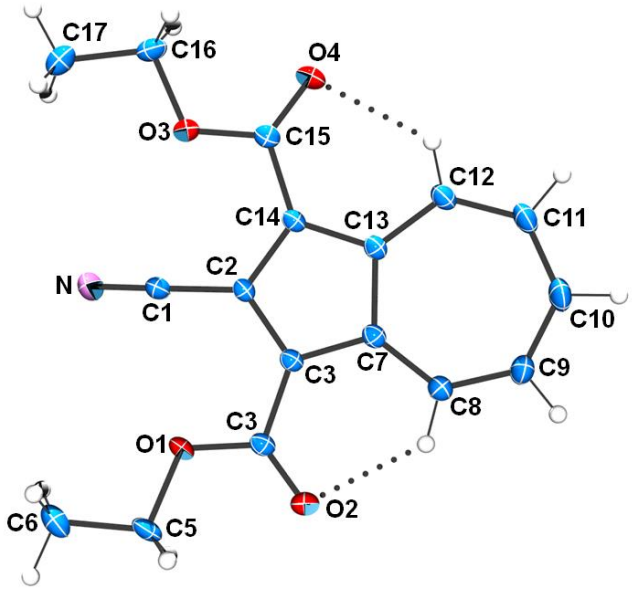


Figure A4.1. X-ray crystal structure of 2-cyano-1,3-diethoxycarbonylazulene generated using ORTEP. Ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): N-C1 1.1438(15), C1-C2 1.4368(14), O2-H8 2.237, O4-H12 2.265, N-C1-C2 176.87(13).

This X-ray diffraction study was conducted by Prof. Nikolay N. Gerasimchuk (Missouri State University - Springfield, MO). A clear, dark-red plate-looking specimen of $C_{17}H_{15}NO_4$, approximate dimensions 0.066 mm x 0.241 mm x 0.614 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1,456 frames were collected. The total exposure time was 8.09 hours. The integration of the data yielded a total of 20,210 reflections to a maximum θ angle of 29.72° (0.72 Å resolution), of which 4,067 were independent (average redundancy 4.969, completeness = 99.7%, Rint = 2.62%) and 3,376 (83.01%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.9272(5) Å, b = 7.7685(4) Å, c = 18.6744(10) Å, β = 95.7020(10)°, volume = 1,433.03(13) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9641 and 1.0000.

The structure was solved and refined using the Bruker SHELXTL Software Package, with Z = 4 for the formula unit, $C_{17}H_{15}NO_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 259 variables converged at R1 = 3.84%, for the observed data and wR2 = 10.40% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.360 e-/Å^3 and the largest hole was -0.223 e-/Å^3 with an RMS deviation of 0.052 e-/Å^3. On the basis of the final model, the calculated density was 1.378 g/cm^3 and F(000), 624 e-. All H-atoms in the structure were objectively found on the electron difference map.

1) K. J. Scheetz, Ph.D. Dissertation, University of Kansas, **2013**.

Table A4.1. Sample and crystal data for 2-cyano-1,3-diethoxycarbonylazulene.

Identification code	NG_837_MBar_ADS_3_127	
Chemical formula	$C_{17}H_{15}NO_4$	
Formula weight	297.30	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal size	0.066 x 0.241 x 0.614 mm	
Unit cell dimensions	a = 9.9272(5) Å	α = 90°
	b = 7.7685(4) Å	β = 95.7020(10)°
	c = 18.6744(10) Å	γ = 90°
Volume	1433.03(13) Å^3	
Z	4	
Density (calculated)	1.378 g/cm^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	624	
Theta range for data collection	2.19 to 29.72°	
Index ranges	-13<=h<=13, -10<=k<=10, -26<=l<=25	
Reflections collected	20210	
Independent reflections	4067 [R(int) = 0.0262]	
Max. and min. transmission	1.0000 and 0.9641	
Structure solution technique	direct methods	
Structure solution program	SHELXS-1013 (Sheldrick, 2013)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4067 / 0 / 259	

Goodness-of-fit on F^2	1.048
Δ/σ_{max}	0.001
Final R indices	3376 data; $I>2\sigma(I)$ R1 = 0.0384, wR2 = 0.0943
	all data R1 = 0.0488, wR2 = 0.1040
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0487P)^2+0.4938P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.360 and -0.223 eÅ^{-3}
R.M.S. deviation from mean	0.052 eÅ^{-3}

Table A4.2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 2-cyano-1,3-diethoxycarbonylazulene.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.01666(11)	0.67556(15)	0.87727(6)	0.0207(2)
C2	0.96327(10)	0.68778(13)	0.94584(5)	0.01521(19)
C3	0.02687(10)	0.77392(13)	0.00663(5)	0.01544(19)
C4	0.16452(10)	0.84788(13)	0.01448(5)	0.0169(2)
C5	0.36971(11)	0.87538(16)	0.96119(7)	0.0244(2)
C6	0.42358(13)	0.83511(19)	0.89055(8)	0.0311(3)
C7	0.93679(10)	0.77002(13)	0.06110(5)	0.01623(19)
C8	0.96087(11)	0.84661(15)	0.12875(6)	0.0215(2)
C9	0.87806(12)	0.84994(18)	0.18443(6)	0.0277(3)
C10	0.75154(12)	0.77534(18)	0.18797(6)	0.0286(3)
C11	0.67340(12)	0.68096(16)	0.13615(6)	0.0257(2)
C12	0.70112(11)	0.63614(15)	0.06701(6)	0.0206(2)
C13	0.81554(10)	0.67489(13)	0.03194(5)	0.01628(19)
C14	0.83508(10)	0.62597(13)	0.96071(5)	0.01559(19)
C15	0.73929(10)	0.52559(13)	0.91181(6)	0.0175(2)
C16	0.70787(12)	0.38893(15)	0.79757(6)	0.0233(2)
C17	0.78707(13)	0.37060(17)	0.73332(6)	0.0268(2)
N1	0.05536(11)	0.67190(17)	0.82161(6)	0.0355(3)
O1	0.23151(7)	0.81145(11)	0.95747(4)	0.02167(17)
O2	0.21378(8)	0.92923(11)	0.06602(4)	0.02429(18)
O3	0.79425(8)	0.48106(10)	0.85193(4)	0.02051(17)
O4	0.62523(8)	0.48607(12)	0.92314(5)	0.0277(2)

Table A4.3. Bond lengths (Å) for 2-cyano-1,3-diethoxycarbonylazulene.

C1-N1	1.1438(15)	C1-C2	1.4368(14)
C2-C3	1.4117(14)	C2-C14	1.4133(13)
C3-C7	1.4199(14)	C3-C4	1.4762(14)
C4-O2	1.2131(13)	C4-O1	1.3403(12)
C5-O1	1.4542(13)	C5-C6	1.5048(17)
C5-H5A	0.993(15)	C5-H5B	0.988(15)
C6-H6A	0.992(18)	C6-H6B	0.988(18)
C6-H6C	0.979(18)	C7-C8	1.3953(15)
C7-C13	1.4701(14)	C8-C9	1.3885(15)
C8-H8	0.955(15)	C9-C10	1.3907(17)
C9-H9	0.957(16)	C10-C11	1.3880(18)
C10-H10	0.970(17)	C11-C12	1.3909(16)
C11-H11	0.946(17)	C12-C13	1.3991(14)
C12-H12	0.946(15)	C13-C14	1.4152(14)
C14-C15	1.4743(14)	C15-O4	1.2120(13)
C15-O3	1.3375(12)	C16-O3	1.4509(13)
C16-C17	1.5052(17)	C16-H16A	0.989(15)
C16-H16B	0.993(16)	C17-H17A	0.983(18)
C17-H17B	0.946(19)	C17-H17C	0.971(18)

Table A4.4. Bond angles (°) for 2-cyano-1,3-diethoxycarbonylazulene.

N1-C1-C2	176.87(13)	C3-C2-C14	110.03(9)
C3-C2-C1	124.95(9)	C14-C2-C1	124.87(9)
C2-C3-C7	107.63(9)	C2-C3-C4	126.87(9)
C7-C3-C4	125.44(9)	O2-C4-O1	123.20(9)
O2-C4-C3	125.29(10)	O1-C4-C3	111.50(9)
O1-C5-C6	107.63(10)	O1-C5-H5A	107.0(9)
C6-C5-H5A	112.9(9)	O1-C5-H5B	107.4(9)
C6-C5-H5B	113.0(8)	H5A-C5-H5B	108.5(12)
C5-C6-H6A	108.8(10)	C5-C6-H6B	110.7(10)
H6A-C6-H6B	108.2(14)	C5-C6-H6C	109.3(10)
H6A-C6-H6C	110.4(14)	H6B-C6-H6C	109.4(14)
C8-C7-C3	125.17(10)	C8-C7-C13	127.59(9)
C3-C7-C13	107.22(9)	C9-C8-C7	128.69(11)
C9-C8-H8	117.0(9)	C7-C8-H8	114.3(9)
C8-C9-C10	129.24(11)	C8-C9-H9	115.8(10)
C10-C9-H9	114.9(10)	C11-C10-C9	129.18(11)
C11-C10-H10	114.9(10)	C9-C10-H10	115.9(10)
C10-C11-C12	129.12(11)	C10-C11-H11	115.9(10)

C12-C11-H11	114.9(10)	C11-C12-C13	128.71(11)
C11-C12-H12	116.3(9)	C13-C12-H12	115.0(9)
C12-C13-C14	125.15(10)	C12-C13-C7	127.42(10)
C14-C13-C7	107.43(8)	C2-C14-C13	107.68(9)
C2-C14-C15	126.58(9)	C13-C14-C15	125.74(9)
O4-C15-O3	123.11(10)	O4-C15-C14	125.60(10)
O3-C15-C14	111.29(8)	O3-C16-C17	106.57(9)
O3-C16-H16A	108.4(9)	C17-C16-H16A	112.8(9)
O3-C16-H16B	108.6(9)	C17-C16-H16B	112.8(9)
H16A-C16-H16B	107.5(13)	C16-C17-H17A	111.2(10)
C16-C17-H17B	109.9(11)	H17A-C17-H17B	109.2(15)
C16-C17-H17C	111.7(10)	H17A-C17-H17C	107.1(14)
H17B-C17-H17C	107.5(15)	C4-O1-C5	115.47(8)
C15-O3-C16	116.79(8)		

Table A4.5. Torsion angles (°) for 2-cyano-1,3-diethoxycarbonylazulene.

C14-C2-C3-C7	-1.06(11)	C1-C2-C3-C7	174.79(10)
C14-C2-C3-C4	176.17(9)	C1-C2-C3-C4	-7.98(17)
C2-C3-C4-O2	175.85(10)	C7-C3-C4-O2	-7.39(17)
C2-C3-C4-O1	-5.33(14)	C7-C3-C4-O1	171.43(9)
C2-C3-C7-C8	-177.81(10)	C4-C3-C7-C8	4.91(16)
C2-C3-C7-C13	1.04(11)	C4-C3-C7-C13	-176.24(9)
C3-C7-C8-C9	179.39(12)	C13-C7-C8-C9	0.77(19)
C7-C8-C9-C10	1.5(2)	C8-C9-C10-C11	-1.6(2)
C9-C10-C11-C12	0.0(2)	C10-C11-C12-C13	0.1(2)
C11-C12-C13-C14	-179.10(11)	C11-C12-C13-C7	1.67(19)
C8-C7-C13-C12	-2.51(18)	C3-C7-C13-C12	178.68(10)
C8-C7-C13-C14	178.16(10)	C3-C7-C13-C14	-0.66(11)
C3-C2-C14-C13	0.64(11)	C1-C2-C14-C13	-175.21(10)
C3-C2-C14-C15	-178.27(9)	C1-C2-C14-C15	5.88(17)
C12-C13-C14-C2	-179.33(10)	C7-C13-C14-C2	0.03(11)
C12-C13-C14-C15	-0.42(17)	C7-C13-C14-C15	178.94(9)
C2-C14-C15-O4	-173.40(11)	C13-C14-C15-O4	7.89(17)
C2-C14-C15-O3	6.90(15)	C13-C14-C15-O3	-171.81(9)
O2-C4-O1-C5	0.38(15)	C3-C4-O1-C5	-178.47(9)
C6-C5-O1-C4	-175.38(10)	O4-C15-O3-C16	3.28(15)
C14-C15-O3-C16	-177.01(9)	C17-C16-O3-C15	174.15(9)

Table A4.6. Anisotropic atomic displacement parameters (Å^2) for 2-cyano-1,3-diethoxycarbonylazulene.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

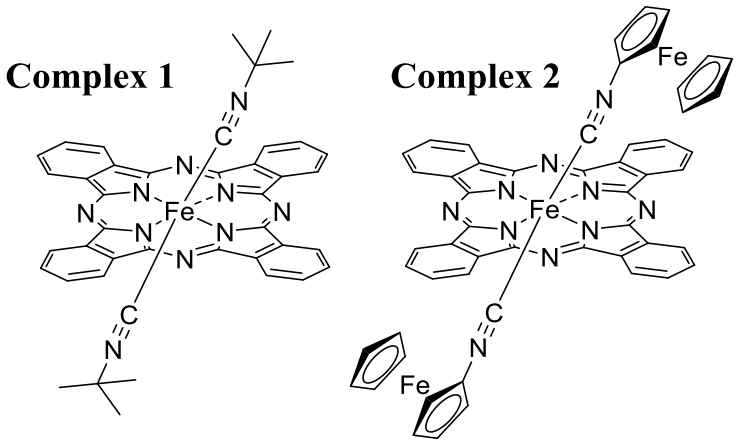
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0152(5)	0.0268(5)	0.0202(5)	-0.0015(4)	0.0022(4)	-0.0041(4)
C2	0.0133(4)	0.0163(4)	0.0163(4)	0.0025(3)	0.0027(3)	0.0009(3)
C3	0.0131(4)	0.0165(4)	0.0167(4)	0.0018(3)	0.0014(3)	0.0000(3)
C4	0.0135(4)	0.0179(5)	0.0190(5)	0.0030(4)	0.0008(3)	0.0001(3)
C5	0.0126(5)	0.0300(6)	0.0310(6)	0.0017(5)	0.0045(4)	-0.0050(4)
C6	0.0218(6)	0.0363(7)	0.0373(7)	0.0023(5)	0.0131(5)	-0.0012(5)
C7	0.0138(4)	0.0173(4)	0.0177(5)	0.0019(4)	0.0018(3)	0.0013(3)
C8	0.0178(5)	0.0266(5)	0.0204(5)	-0.0023(4)	0.0032(4)	-0.0012(4)
C9	0.0242(6)	0.0398(7)	0.0195(5)	-0.0072(5)	0.0050(4)	-0.0011(5)
C10	0.0246(6)	0.0411(7)	0.0219(5)	-0.0020(5)	0.0104(4)	0.0017(5)
C11	0.0191(5)	0.0346(6)	0.0250(6)	0.0016(5)	0.0095(4)	-0.0019(4)
C12	0.0155(5)	0.0242(5)	0.0226(5)	0.0016(4)	0.0047(4)	-0.0017(4)
C13	0.0138(4)	0.0177(4)	0.0176(5)	0.0017(3)	0.0027(3)	0.0009(3)
C14	0.0122(4)	0.0168(4)	0.0178(5)	0.0017(4)	0.0019(3)	-0.0003(3)
C15	0.0157(4)	0.0168(5)	0.0197(5)	0.0022(4)	0.0010(4)	0.0000(3)
C16	0.0217(5)	0.0242(5)	0.0230(5)	-0.0045(4)	-0.0032(4)	-0.0042(4)
C17	0.0318(6)	0.0270(6)	0.0210(5)	-0.0044(4)	-0.0011(4)	0.0000(5)
N1	0.0273(5)	0.0567(7)	0.0237(5)	-0.0070(5)	0.0092(4)	-0.0142(5)
O1	0.0128(3)	0.0295(4)	0.0234(4)	-0.0025(3)	0.0049(3)	-0.0045(3)
O2	0.0193(4)	0.0303(4)	0.0229(4)	-0.0038(3)	0.0004(3)	-0.0059(3)
O3	0.0173(4)	0.0249(4)	0.0191(4)	-0.0039(3)	0.0008(3)	-0.0039(3)
O4	0.0167(4)	0.0375(5)	0.0293(4)	-0.0052(4)	0.0041(3)	-0.0091(3)

Table A4.7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 2-cyano-1,3-diethoxycarbonylazulene.

	x/a	y/b	z/c	U(eq)
H8	1.0442(15)	0.9086(19)	1.1360(7)	0.026(4)
H9	0.9110(16)	0.915(2)	1.2259(9)	0.037(4)
H10	0.7106(17)	0.794(2)	1.2324(9)	0.038(4)
H11	0.5885(17)	0.643(2)	1.1490(9)	0.035(4)
H12	0.6331(15)	0.5732(19)	1.0392(8)	0.025(3)
H5A	1.4212(15)	0.8175(19)	1.0027(8)	0.027(4)
H6A	1.5180(18)	0.878(2)	0.8921(9)	0.040(4)

	x/a	y/b	z/c	U(eq)
H16A	0.6233(16)	0.4553(19)	0.7868(8)	0.030(4)
H17A	0.8702(19)	0.304(2)	0.7453(9)	0.046(5)
H5B	1.3669(15)	1.000(2)	0.9713(8)	0.027(4)
H6B	1.4243(17)	0.710(2)	0.8821(9)	0.041(4)
H16B	0.6832(16)	0.276(2)	0.8178(8)	0.033(4)
H17B	0.8101(18)	0.481(2)	0.7166(9)	0.046(5)
H6C	1.3665(18)	0.891(2)	0.8515(9)	0.042(5)
H17C	0.7352(18)	0.312(2)	0.6938(9)	0.046(5)

Appendix 5. EPR of Iron(II) Phthalocyanine Motifs Axially Coordinated with Two CNR (R = ferrocenyl, *tert*-butyl) Ligands



Synthesis of complexes **1** and **2** were carried out according to Ref. 1. EPR was carried out on an X-band Bruker EMX Plus spectrometer with a dual mode cavity operating in perpendicular mode using an Oxford Cryostat at 77K. Spectra were acquired and baseline corrected using Xenon (v.1.1b.44).

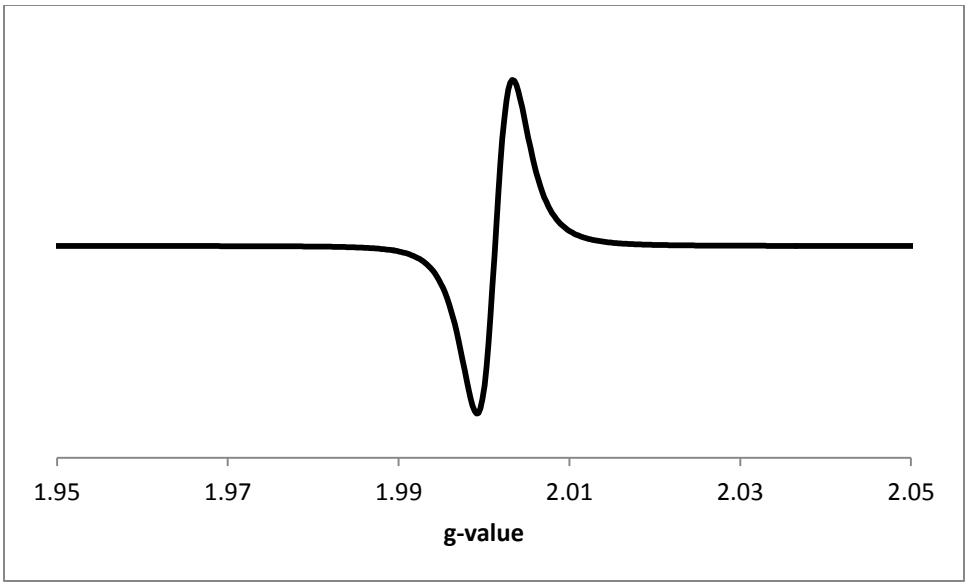


Figure A5.1. EPR spectrum of complex **1** at 77K. g_{iso} = 2.0013.

In an inert atmosphere dry box, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone [DDQ] (1.9 mg, 0.008 mmol) was dissolved in 5 mL CH_2Cl_2. 0.85 mL of DDQ solution was added to complex **1** (5.2 mg, 0.007 mmol) in 5 mL CH_2Cl_2 and mixed at 25°C. A small aliquot was transferred to an EPR tube and sealed with a tied-off piece of tygon tubing. The sample was removed from the dry box and immediately frozen in $N_2(l)$. The EPR spectrum was taken within 1 hour of generating the sample see Figure A5.1. EPR acquisition parameters: attenuation = 30 dB, microwave power = 0.200 mW, frequency = 9.64 GHz, sweep width = 1,000 G, modulation amplitude = 4.0 G, modulation frequency = 100 kHz, gain = 30 dB, conversion time = 4.02 ms, time constant = 0.08 ms, and resolution = 2,500 points.

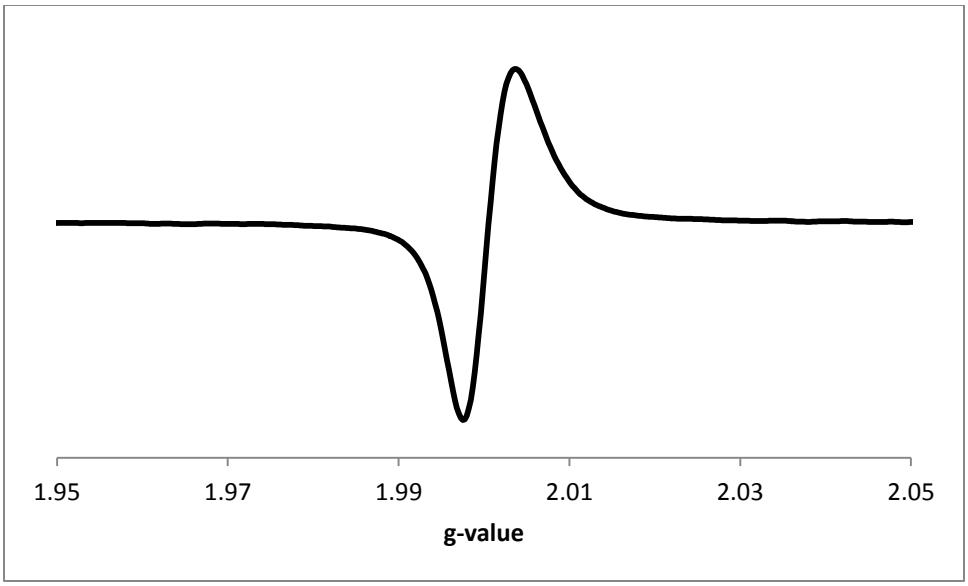


Figure A5.2. EPR spectrum of complex **2** at 77K. g_{iso} = 2.0005.

In an inert atmosphere dry box, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone [DDQ] (1.9 mg, 0.008 mmol) was dissolved in 5 mL CH_2Cl_2. 0.30 mL of DDQ solution was added to complex **2** (1.0 mg, 0.001 mmol) in 2 mL CH_2Cl_2 and mixed at 25°C. A small aliquot was transferred to an EPR tube and sealed with a tied-off piece of tygon tubing. The sample was removed from the dry box and immediately frozen in $N_2(l)$. The EPR spectrum was taken within 1 hour of generating the sample, see Figure A5.2. EPR acquisition parameters: attenuation = 26 dB, microwave power = 0.502 mW, frequency = 9.64 GHz, sweep width = 1,000 G, modulation amplitude = 4.0 G, modulation frequency = 100 kHz, gain = 30 dB, conversion time = 4.02 ms, time constant = 0.08 ms, and resolution = 2,500 points.

1) Nemykin, V. N.; Purchel, A. A.; Spaeth, A. D.; Barybin, M. V. *Inorg. Chem.* **2013**, *52*, 11004.